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GASReP PRESSC

1st Annual
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1er Symposium annuel
sur la restauration des eaux souterraines et des sols contaminés

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The organizing committee would like to record its appreciation of the efforts of the speakers and the moderators.

Le Comité d'organisation du Symposium aimerait remercier les conférenciers et les animateurs de leur précieuse collaboration.

TABLE OF CONTENTS TABLE DES MATIÈRES

section

SESSION 1/1ère SÉANCE

Overview of Canadian Petroleum Products Institute (CPPI) Activities in Groundwater and Soil Remediation (Survol des activités de l'Institut canadien des produits pétroliers (ICCP) en matière de restauration des eaux souterraines et des sols contaminés) ____ 1
Roger Lafleur
Canadian Petroleum Products Institute
Ottawa, Ontario

Canadian Petroleum Association Environment Research Advisory Coucil - Objectives and Research Projects (Conseil consultatif de recherche en environnement de l'Association pétrolière du Canada (APC) - Objectifs et projets de recherche) ____ 2
Brian Croft
Amoco Canada Petroleum Company Ltd
Calgary, Alberta

Current and Recent Research of the American Petroleum Institute (Recherche actuelles et récentes de l'institut du pétrole des États-Unis) ____ 3
Dr. Bruce Bauman
American Petroleum Institute
Washington, D.C.

U.S. Environmental Protection Agency Groundwater and Research, Development and Demonstration Initiatives (Initiatives de l'Environmental Protection Agency des États-Unis en matière de recherche et développement et de démonstration dans le domaine des eaux souterraines) ____ 4
Clinton Hall (USEPA)
R. S. Kerr Lab (RSKERL)
Ada, Oklahoma

TABLE OF CONTENTS (cont'd) TABLE DES MATIÈRES(suite)

section

The Current State-of-the-Art of In-Situ Bioremediation: Considerations, Limitations, Potential and Future Directions (État actuel de la technique de la biorestauration *in situ* : facteurs, limites, potentiel et orientations futures) 5
Dave Major, Ph.D
Beak Consultants Limited
Guelph, Ontario

In-Situ Intercedent Biological Barriers for the Containment and Remediation of contaminated Groundwater (Barrières biologiques *in situ* pour le confinement et la restauration des eaux souterraines contaminées) 6
Kevin Bellamy, Nicole de Lint
ORTECH International
Mississauga, Ontario

D. Roy Cullimor
Abimbola Abiola, Droycon Bioconcepts
Regina, Saskatchewan

SESSION 2/2^e SÉANCE

Nitrate Addition as an Alternate Electron Acceptor for the Remediation of Anaerobic BTEX Contaminated Groundwater (Addition de nitrate comme électroaccepteur auxiliaire pour la restauration des eaux souterraines anaérobies contaminées au BTEX) 7
J. R. Barbaro, J. F. Barker, L. A. Lemon
Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario

TABLE OF CONTENTS (cont'd) **TABLE DES MATIÈRES(suite)**

section

Current, Innovative and Emerging Excavate and Treatment Technologies for Contaminated Sites (Technologies actuelles, novatrices et pointues d'excavation et de traitement des sols contaminés) ____ 8
Paul Beck
INTERA KENTING
Toronto, Ontario

Dennis W. Lafleur, Louis Sabourin
INTERA KENTING
Ottawa, Ontario

Solvent Extraction and Recovery of Petroleum Hydrocarbons from Soil (Extraction des solvants et récupération d'hydrocarbures non gazeux du sol) ____ 9
M. Punt
River Road Environmental Technology Centre
Environment Canada
Ottawa, Ontario

G. Choryhanna
Seprotech Systems
Ottawa, Ontario

L. Fytche
University of Waterloo
Waterloo, Ontario

E. Deschambault
Université de Sherbrooke
Sherbrooke, Quebec

Surface Bioreactors for Cleaning Hydrocarbon Contaminated Soils (Bioréacteurs de surface pour dépolluer les sols contaminés aux hydrocarbures) ____ 10
Lin Callow
Gulf Canada Resources Ltd.
Calgary, Alberta

TABLE OF CONTENTS (cont'd) TABLE DES MATIÈRES(suite)

section

In-Situ Volatilization Technologies R, D, & D Scoping Study (Examen de la portée de la recherche-développement et de la démonstration de la volatilisation *in situ*) ____ 11
Martin Adomait, Brian Wiffin
CH2M HILL ENGINEERING LIMITED
Waterloo, Ontario

SESSION 3/3^e SÉANCE

Literature Review & Research Scoping Study on the Treatment of Volatile Organic Carbon Compounds in the Off-gas from Contaminated Goundwater and Soil Remediation Technologies (Revue de la littérature et examen de la portée des recherches en traitement des composés organiques volatils présents dans les gaz d'échappement provenant des méthodes de restauration des eaux souterraines et des sols contaminés) ____ 12
John Brewer
Ian Martin Associates
Wastewater Technology Centre
Environment Canada
Burlington, Ontario

Iron Pre-treatment for Pump and Treat Systems (Prétraitement au fer pour les systèmes de pompage et de traitement) ____ 13
Mark Halevy
Wastewater Technology Centre
Environment Canada
Burlington, Ontario

TABLE OF CONTENTS (cont'd) TABLE DES MATIÈRES(suite)

section

Site Selection for Demonstrations and Evaluation of Technologies for Remediation of Gasoline Spills (Sélection des emplacements pour la démonstration et l'évaluation des technologies de nettoyage des déversements d'essence) ______________ 14
L. A. Lemon, J. F. Barker
Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario

Remediating Subsurface Contamination Around Sour Gas Processing Facilities: Opportunities for Field Research, Development and Demonstration (Décontamination du sous-sol autour des installations de traitement des gaz acides: possibilités de recherche, du développement et de démonstration sur le terrain) ______________ 15
Paul E. Hardisty, T. L. Dabrowski
Piteau Engineering Ltd.
Calgary, Alberta

The Influence of Methanol and MTBE on the Fate and Persistence of Monoaromatic Hydrocarbons in Groundwater (L'influence du méthanol et du méthoxy-2 butane sur le sort et la persistance des hydrocarbures aromatiques monocycliques dans les eaux souterraines) ______________ 16
J. F. Barker, C. E. Hubbard, L. A. Lemon
Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario

Statistical Method Developed by the American Petroleum Institute to Evaluate the Technical Limits of a Groundwater Remediation Project (Méthode statistique élaborée par l'institut du pétrole des États-Unis en vue de l'évaluation des limites techniques d'un projet de restauration des eaux souterraines) ______________ 17
Bob Hockman (API)
Amoco Corporation
Tulsa, Oklahoma

TABLE OF CONTENTS (cont'd) TABLE DES MATIÈRES(suite)

section

SESSION 4/4^e SÉANCE

Current and Future in-situ Bioremediation Activities
(Activités actuelles et futures en matière de biorestauration *in situ*) ______ 18
John Wilson
R. S. Kerr Lab
Ada, Oklahoma

Chemical Extraction and Solidification R & D Activities
(Activités de R-D en extraction et solidification des produits chimiques) ______ 19
Ed Barth
U.S. EPA Centre for Environmental Research Information
Cincinnati, Ohio

Bioremediation Field Performance Evaluation Initiative
(Projet d'évaluation du rendement sur le terrain de la biorestauration) ______ 20
Walter Kovalick
U.S. EPA Technology Innovation Office
Washington, D.C.

Overview of Canadian Petroleum Products Institute (CPPI) Activities in Groundwater and Soil Remediation

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CURRENT AND RECENT RESEARCH OF THE AMERICAN PETROLEUM INSTITUTE

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The American Petroleum Institute is the trade association for the petroleum industry of the United States. Over 200 member companies and several thousand individual members participate in API's activities in the petroleum industry's operational sectors: exploration, production, refining, transportation, and marketing. During the previous decade, API has played an increasing role in helping the industry to address environmental issues, including soil and groundwater. Historically, API's groundwater research has focused on assessment and remediation of releases of gasoline. Among other topics, early API research examined biodegradation processes in groundwater and soil venting (i.e., vacuum extraction). This work has served to spur considerable additional research into those remediation techniques.

API continues to further its program for research on soil groundwater contamination under the guidance of the Soil/Groundwater Technical Task Force and the Environmental Monitoring Workgroup. Current work spans the areas of assessment, fate and transport, and remediation. A summary of current API research projects follows. A list of recently published API reports is included below.

RECENT API PUBLICATIONS

Abandoned Oil and Gas Wells - A Quantiative Assessment of Their Environental Implications. 1990. API, Washington, D.C.

Evaluation of Analytical Methods for Measuring Appendix IX Constituents in Groundwater. 1989. API, Washington, D.C.

Hydrogeologic Data Base for Groundwater Modeling. 1989. API, Washington, D.C.

Rehabilitation of Groundwater: Removal of Soluble Petroleum Constituents through Soil Application. API, Washington, D.C.

(Note: The following four publications should be available by April, 1991)

Alternative Treatment Technologies for Reducing MTBE and Methanol Concentrations in Groundwater

Cost and Treatment Efficiency for Removal of Dissolved Gasoline Components from Groundwater

Evaluation of Product Plume Delineation Techniques

Sampling and Analysis of Gasoline-Range-Organics in Soils

Note: The above publications are available from API Publication Dept., 1220 L St. NW, Washington, D.C. 20005 (202/682-8375)

CHEMICAL FATE AND TRANSPORT OF OXYGENATES IN GROUNDWATER – GW-16

Objective: To evaluate the impact of oxygenates in gasoline on the fate and transport of BTEX (benzene, toluene, ethylbenzene, and xylene) in groundwater.

Initiated: 1988

Scope: Blends of gasoline and varying amounts of MTBE and methanol will be evaluated in the laboratory to determine oxygenate effects on aqueous solubility, sorptive retardation, and biodegradation of BTEX. In a field study, the fate and transport of contaminated groundwater plumes using gasoline, a methanol/gasoline mixture (85% methanol/15% gasoline), and a 15% MTBE fuel will be compared.

Status/Results: Draft reports have been received for the laboratory cosolubility and sorption studies. Draft final reports for the biodegradation and field studies are expected in October. There was no enhanced cosolubility of BTEX when either methanol or MTBE was present in gasoline up to concentrations of 15%. At higher methanol concentrations, aqueous BTEX concentrations were somewhat higher, but it is uncertain if the same phenomenon would occur in the field. Sorption of BTEX on sands was not significantly altered by the presence of either MTBE or methanol.

Completion Date: February 1991

OXYGENATED FUEL DISSOLUTION, PLUME CHARACTERISTICS, AND SOIL INTERACTIONS – GW-20

Objective: To generate laboratory data regarding the nature of groundwater contamination plumes likely to be created from leaks and spills of oxygenated fuels.

Initiated: 1990 (September)

Scope: In soil column studies, the partitioning of methanol and gasoline into water, simulating an M-85 spill, will be evaluated. The distribution of BTEX among the aqueous, methanol, and gasoline phases will be evaluated in batch experiments. Studies using a thin layer of sand between two parallel glass plates will provide visual confirmation of methanol/gasoline interactions with water. Additional work will be performed to characterize the surface tension relationships between methanol/water mixtures and air.

Status/Results: Laboratory work will be completed by March 1991, and a draft final report will be submitted by May 1991.

Completion Date: September 1991

EVALUATION OF DETECTION TECHNIQUES – GW-2

Objective: To determine the relative effectiveness of various soil gas and geophysical detection techniques for delineating subsurface hydrocarbon groundwater plumes.

Initiated: 1987

Scope: Literature and manufacturers' information on the performance of different detection techniques (various active and passive soil gas methods, ground penetrating radar, earth contact resistivity, and electromagnetic methods) were compared with field-collected data for their sensitivity, reliability, and reproducibility for detecting benzene, toluene, and xylenes in the vadose zone. Contour maps were produced to give a visual representation of the plume characteristic. Each technique was evaluated on its ability to characterize subsurface hydrocarbon plumes and its suitability for specific field applications.

Status/Results: The field study has been completed by the contractor. All of the detection techniques performed well and, as expected, gave varying degrees of hydrocarbon detection capability. Comments on the second draft final report will be sent to the contractor shortly.

Completion Date: December 1990

LEAK DETECTION METHODS FOR PRODUCTION TANKS – GW-24

Objective: Determine the unique characteristics of crude oil releases at aboveground production tank systems to provide data for discussion during development of future federal or state aboveground storage tank legislation and regulations.

Initiated: 1990 (June)

Scope: Contractor will develop an approach for characterizing crude oil releases from oil production storage tank systems and describe the nature of releases at several field sites. Approximately 5-10 production sites that are being decommissioned will be selected for detailed field examination to sample and describe hydrocarbon releases that have occurred from the tank system. The type of tank construction and installation will be noted, along with other equipment parameters of interest (e.g., size, age, and presence of perforations). Soil samples will be taken to assess the nature of the movement of crude oil from the tank bottom or from other types of spills. Information will be interpreted regarding implications for detection of crude oil leakage from production tanks.

Status/Results: Four sites have been sampled through August. Up to six additional sites will be sampled in September and October. Draft final report expected November 30; final report expected January 31, 1991.

Completion Date: March 1991

NATURAL AND NONPOINT-SOURCE BTX LEVELS IN SOILS – GW-7

Objective: To determine the range in concentration of water-extractable natural and nonpoint-source BTX levels in soil samples collected from selected sites in the U.S.

Initiated: 1987

Scope: The levels of BTX from naturally occurring, uncontaminated, and nonspill-contaminated soils are not known. The contractor will attempt to quantify ambient hydrocarbon levels in selected soil types from different areas of the country.

Status/Results: An initial round of sampling and analysis has been completed. Preliminary results indicated that at a quantification detection limit of 40 ppt, no quantifiable hydrocarbons could be found in samples collected at selected field sites. A review of the findings indicated that no significant benefit would be derived from completing the remaining tasks of the study, and a decision was reached to terminate this project. However, it was determined that the information obtained to date would be of value to the industry; therefore, a final report was prepared on the work completed to date, and the contract terminated. The final report was received in late August and is being balloted.

Completion Date: November 1990

SAMPLING AND ANALYSIS OF SOILS FOR GASOLINE RANGE ORGANICS – GW-1

Objective: To identify and test appropriate sampling and analysis methods suitable for determining low levels of gasoline constituents in the soil.

Initiated: 1987

Scope: Using results from a literature survey on specific sampling and analytical methods, a workshop of experts will help identify promising approaches worthy of further investigation. In the laboratory, the performance of several sampling and analytical methods for BTEX and total hydrocarbons will be evaluated using several soil types spiked with an artificial gasoline mix. Finally, both fresh and weathered gasoline samples will be obtained from the field and analyzed in the laboratory to confirm real-world applicability of these methods.

Status/Results: A new method has been developed and approved for distribution. Comments on the final report are being incorporated by the contractor. The method incorporates field methanol extraction in a VOA vial that can be directly analyzed by purge-and-trap

GC/PID (i.e., without further manipulation of the field sample). Total petroleum hydrocarbons can also be determined by coupling a FID in series with the PID.

The purge-and-trap method has a lower detection limit (less than 100 ppb), but its dynamic range is limited on the high end (i.e., it is too sensitive to handle soils with the higher levels of contamination commonly found in field situations). A screening technique may be necessary as a first step. Work on an additional method to analyze distillate-range organics in soil is being initiated with the EPA Office of Underground Storage Tanks.

Completion Date: November 1990

ASSESSMENT OF IMPACT OF RESIDUAL HYDROCARBONS IN SOILS OVER GROUNDWATER -- GW-6

Objective: To assess the potential for groundwater contamination by examining the relationship between the mass of hydrocarbon contaminants adsorbed to the soil in the vadose zone and the concentration of hydrocarbons in water that has been leached through the contaminated soil.

Initiated: 1987

Scope: Cleanup criteria for motor-fuel-contaminated soils are often based on estimates of groundwater contamination caused by leaching of contaminants from the soils. However, there are no documented studies that determined the extent of such leaching. This laboratory project will determine, for several soil types, the threshold level of hydrocarbons below which percolating water will not leach significant levels of hydrocarbons into underlying groundwater. Soil cores from hydrocarbon spill sites will be analyzed for their concentrations of BTEX and total hydrocarbons. Leachate will be analyzed for total hydrocarbons and BTEX over several pore volumes to determine the potential for groundwater contamination and the long-term release of BTEX from soil. TCLP analyses of the soil cores will be compared to the water leachate results.

Status/Results: A total of 36 soil cores were collected from three sites. Difficulty in quantifying the amount of hydrocarbon in the soil cores before leaching resulted in an inability to establish a quantitative relationship between soil BTX and leachate quality. There was no correlation between TCLP leachate and water leachate from the same soils. Final comments on the draft report are in progress.

Completion Date: December 1990

MEASUREMENT OF MOTOR-FUEL-CONTAMINATED SOIL LEACHATE -- GW-17B

Objective: To develop a standard leaching protocol for use in assessing the potential for groundwater contamination from motor-fuel-contaminated soils.

Initiated: October (1990)

Scope: Phase I will evaluate different methodologies for characterizing the leaching of hydrocarbon from contaminated soil using column studies, TCLP, and modified TCLP batch extraction procedures. Three different soil types (sandy, silty, and clayey) will be screened. Focus is on soils that have been treated (e.g., vacuum extraction and bioremediation) or that have low levels of residual contamination (e.g., less than 1000-ppm TPH). Soils and leachate will be analyzed for BTEX, MTBE, and other hydrocarbons. Correlations between soil contaminant concentrations and leachate contaminant concentrations will be made. Soil samples will also be characterized by field analytical methods (e.g., soil headspace) and results correlated with leachate concentrations. Phase

I will provide a recommendation for a standard leachate generation and characterization protocol that will be used to evaluate at least 10 additional soils (Phase II). Results from Phase II should provide guidance for the determination of soil cleanup standards.

Status/Results: Samples for Phase I to be collected in November 1990; work to be completed by April 1991. Phase II work to be initiated in May 1991.

Completion Date: October 1991

SUBSURFACE MONITORING DATA FOR ASSESSING IN-SITU BIODEGRADATION OF AROMATIC HYDROCARBONS (BTEX) IN GROUNDWATER -- GW-25A

Objective: Demonstrate that field measurement methods can be used to determine rates of BTEX biodegradation in dissolved groundwater plumes so that regulatory permission can be obtained for "passive" bioremediation at fuel spill sites.

Initiated: 1991 (January)

Scope: A gasoline spill site will be identified and characterized for pertinent chemical and physical properties. Groundwater and soil gas samples will be obtained on a monthly basis and analyzed for key inorganic and organic parameters (e.g., CO2, O2, BTEX, etc.) for 18 months. The indirect measurements of subsurface biological activity will be compared with predicted movement of BTEX in the dissolved plume to see if they provide reasonable estimates of natural biodegradation rates of BTEX in groundwater. Laboratory leaching studies and microcosm biodegradation studies will be conducted to complement the field study. Several modeling approaches will be evaluated for their ability to successfully predict rates of natural attenuation of BTEX.

Status/Results: Initial meeting with contractor to review potential sites to occur on January 10, 1991.

Completion Date: May 1993

THE ANAEROBIC DECOMPOSITION OF BENZENE IN ANOXIC AQUIFER SLURRIES -- WM-11 (GW-19)

Objective: Evaluate EPA anaerobic biodegradation protocol; develop alternative monitoring techniques for anaerobic microcosms; characterize low oxygen concentration benzene biodegradation.

Initiated: 1989

Scope: Additional funding in 1990 is to allow: 1) continued monitoring of anaerobic microcosms through 24 months, 2) initial site reconnaissance for obtaining samples at second site and setting up microcosms for that site, and 3) additional sampling at original site to evaluate seasonal effects (i.e., temperature) on microbial community and benzene biodegradation. Additional work ($118K) in 1992 is anticipated to complete the work for the second site and work on the anaerobic biodegradation of gasoline, pending approval of the API project team.

Status/Results: To date, the following progress has been made towards completion of the original proposal:

1) The evaluation of the EPA protocol (i.e., a critical evaluation of its practicality and implementabilty) has been completed. Numerous problems in the execution of the protocol were noted and alternatives suggested/implemented.
2) The evaluation of an alternative method for monitoring the microcosms has also been completed and has shown that the method (using pressure transducers to provide continuous monitoring) is effective. A meeting with the EPA authors of the protocol will occur in late 1990 or early 1991 to present these results. It is hoped that this meeting will lead to a decision by EPA to modify the protocol in accordance with the findings of the API study.
3) Samples have been obtained and microcosms established for the study to assess benzene biodegradation at low (less than 2 ppm) oxygen concentrations.

Execution of the full protocol requires samples from six sites. Only one site has been sampled so far. Two other sites will be sampled in 1991.

Completion Date: June 1993

AN ASSESSMENT MODEL FOR VENTING GASOLINE-RANGE HYDROCARBONS IN SOILS – WM-7 (GW-18)

Objective: To optimize the design and operation of soil venting systems for cleaning up gasoline-contaminated soils through the development of a simulation model.

Initiated: 1989

Scope: Contractor will develop a three-dimensional, multiphase, compositional transport model. The model will be designed to simulate hydrocarbon transport and microbial degradation under general venting scenarios, simulating the mass flow of air through the soil, the transfer of volatile hydrocarbons from the liquid phase to the vapor phase, and the biodegradation of less volatile hydrocarbons (enhanced biodegradation due to increased oxygen provided during venting is a likely synergistic effect of venting but has not been quantified). Of particular importance will be the modeling of these processes at the capillary fringe where high-moisture conditions complicate both modeling and hydrocarbon removal. A preprocessor will be developed to facilitate site-specific input required by the transport model. The transport model will be verified through comparison with field data from a USGS field research site. A method to optimize venting system design (i.e., number, location, and pumping rates for venting wells) will also be developed.

Status/Results: Work has been initiated on the characterization of the field site and adaptation of the USGS MODFLOW model to airflow modeling. Decision variables and cost information are being collected for the venting optimization model. Field experiments were conducted over the summer and fall months to validate the venting flow and transport model, including effects on biodegradation. Draft final report expected in March 1991.

Completion Date: August 1991

DEVELOPMENT OF WASTE AND DISPOSAL PRACTICE-SPECIFIC GROUNDWATER MODELS – GW-22

Objective: To develop information to provide API with documentation on the impropriety of the EPA Toxicity Characteristic Rule's failure to provide for a separate treatment for wastewaters managed in surface impoundments, and to demonstrate that EPA should consider specific modeling scenarios for certain large-volume waste management practices (including nonhazardous waste impoundments).

Initiated: 1990 (July)

Scope: Phase I will evaluate EPA's comparison of the dilution/attenuation factors (DAFs) developed for the Toxicity Characteristic Rule (focusing on benzene) using the EPACML and EPACMS models, including the modeling assumptions used, and validate the input data. In Phase II, the contractor will conduct a survey on petroleum industry surface impoundments to develop a hydrogeologic database that can be used as more realistic input to these models to provide a better estimate of potential exposures to contaminants released from surface impoundments.

Status/Results: A preliminary report on Phase I is due in October, and a draft final report is due by November 30, 1990. The EPA model has been thoroughly reviewed, and key input parameters and assumptions identified. The survey form is in development, and specific companies are being contacted to identify those facilities that will be included in the survey.

Completion Date: March 1991

MODELING OXYGEN TRANSPORT-LIMITED BIODEGRADATION IN GROUNDWATER – GW-14B

Objective: To provide an improved ability to accurately model the biodegradation of benzene and other soluble hydrocarbons in groundwater.

Initiated: 1988

Scope: The study will begin with a literature review of field and laboratory biodegradation rate data for petroleum hydrocarbons in groundwater, including information on dissolved oxygen concentrations, groundwater temperature, aquifer characteristics, and contaminant concentrations. This information will be used to help develop and verify a three-dimensional numerical model that will predict oxygen-limited biodegradation rates of soluble hydrocarbon plumes into heterogeneous groundwater systems and the role of oxygen transport in the biodegradation process. Dr. Kemblowski (Utah State University) will serve as advisor/reviewer to this project. He will review progress and draft reports and participate in meetings with the contractor.

Status/Results: The initial literature review has been evaluated but will not be finalized until project completion to allow continual updating as relevant research is published. Work has begun on the numerical and analytical solutions required (Phase II). Phase III will involve computer simulation of the theoretical approach developed in Phase II. Because of the complexity of the modeling effort, a Cray 2 supercomputer will be utilized. Code development for the Cray has also been initiated.

Completion Date: June 1991

ALTERNATIVE TREATMENT TECHNOLOGIES FOR REDUCING MTBE AND METHANOL CONCENTRATIONS IN GROUNDWATER – GW-8

Objective: To identify alternative technologies for reducing methyl tertiary butyl ether (MTBE) and methanol to trace levels in groundwater and to evaluate their cost-effectiveness.

Initiated: 1987

Scope: Because of the high cost associated with hydrocarbon cleanup from groundwater, an earlier study attempted to optimize treatment efficiencies for the removal of hydrocarbons and ethers to below 1 ppb from groundwater by using carbon adsorption and air stripping. The present study focused on oxygenated fuels cleanup by examining more cost-effective technologies as alternatives to conventional treatment technologies. Methanol was added as a component of interest.

Status/Results: The literature review on alternate removal technologies for MTBE and methanol has been completed and is being published as a stand-alone document. The contractor has recommended the use of UV-catalyzed oxidation for further laboratory testing over other treatment methods. An additional $15K has been approved to fund other tasks and to perform methanol treatment using the same chemical oxidation methodology. Pilot testing of both chemicals has been completed, and a draft final report is expected in October.

Completion Date: January 1991

AN EVALUATION OF ON-SITE SOIL TREATMENT TECHNOLOGIES – GW-17A

Objective: To compare the effectiveness of existing on-site remediation technologies for soils contaminated with mid- and light-boiling hydrocarbons.

Initiated: 1989

Scope: This multiphase project entails a review and selection of approximately three on-site soil remediation technologies for an actual field demonstration of their effectiveness at an inactive Chevron fuel terminal in Tacoma, WA. The 3-acre site will be fully characterized for variations in hydrocarbon concentrations in the soil and subsurface matrix differences. Using a randomized block design, soil plots will be assigned to each technology for decontamination. Both total petroleum hydrocarbons and selected hydrocarbon indicator constituents will be monitored for treatment effectiveness.

Status/Results: The contractor has initiated a review of published information on currently available soil cleanup technologies and has completed the site characterization task. The contractor has performed an engineering assessment of potentially useful technologies for selection as candidates for on-site hydrocarbon decontamination. Eight different bioremediation methods and two thermal treatment methods will be evaluated. Three control plots have also been established. Soil samples are to be taken at the beginning of treatment, at intervals during treatment, and at the completion of the treatment method to assess the effectiveness for removing BTEX and selected PNAs from soils. A draft final report is due in January 1991.

Completion Date: April 1991

COST AND TREATMENT EFFICIENCY FOR REMOVAL OF DISSOLVED GASOLINE COMPONENTS FROM GROUNDWATER – GW-3 (GTI)

Objective: To document from actual cases the cost-effectiveness of carbon adsorption and air stripping techniques for removing dissolved hydrocarbons and ethers from groundwater.

Initiated: 1987

Scope: The contractor compiled case histories of sites where air stripping, carbon adsorption, or both have been used to reduce gasoline component concentrations to trace levels. Engineering design data, influent and effluent concentrations of BTX and ethers (MTBE and isopropylether), and capital and operating costs were compiled and verified for up to 50 cleanup sites. Estimation of cleanup efficiencies were carried out by comparing contaminant concentrations before and after treatment. The project is jointly funded and managed with API's Marketing Department.

Status/Results: A wide range of costs associated with groundwater treatment was found. Median costs for air stripping systems of 10-50 gpm are $2.80/1000 gallons. Operating costs are approximately 40% greater than design costs, partially attributable to operating flow rates that are much lower than the design flow rates. Site-specific factors and engineering design differences appear to contribute to some of the cost variability when comparing the use of air stripping at different sites. Air stripping generally achieved 99% removal of benzene. MTBE removal ranged from 56%-99%. The final report is being reviewed and balloted.

Completion Date: November 1990

EXPOSURE/RISK ASSESSMENT FRAMEWORK FOR THE MANAGEMENT OF SUBSURFACE CONTAMINANTS -- GW-21

Objective: To develop a computerized, decision-based framework to assess site-specific target or clean-up levels and corresponding exposure potentials, thereby facilitating decision-making in establishing clean-up requirements.

Initiated: 1990 (September)

Scope: A software system is to be developed to provide chemical fate/transport, exposure, and environmental impact/risk analysis of sites at which petroleum hydrocarbon releases have occurred. Based on user inputs, the software system is to estimate exposure levels and potential risks/environmental impacts corresponding to user-specific site- and chemical-specific target or clean-up levels. The software system is to specify statistical confidence intervals on the derived exposure levels and assess the significance of the exposure levels in relation to existing environmental and human health criteria/standards.

Status/Results:

- Contractor selection and contract awarded 10/90.
- Letter report to be submitted 2/1/91 providing contractor review of the Petroleum Release Decision Framework (PRDF) and assessing applicability of the PRDF logic to development of the exposure/risk assessment framework.
- Interim report due 5/1/91 describing contractor development of exposure/risk assessment modules, including hazard identification, source characterization, dose/response, pathway analysis and uptake modules, and the uncertainty analysis component.
- Draft user's manual and software to be submitted 11/1/91, providing the exposure/risk assessment software system and accompanying system documentation.
- Final user's manual and software due 3/1/92, incorporating comments from beta testing of the draft software system.

Completion Date: March 1992

FIELD EVALUATION OF SOIL VENTING -- GW-13

Objective: To investigate the ability of in situ soil venting to remove soluble hydrocarbons to the extent that residual levels will not adversely impact groundwater.

Initiated: 1988

Scope: The contractor will conduct in situ venting of petroleum hydrocarbons at two field sites in California. The characteristics of the two sites are sufficiently different that review of engineering parameters used and the results obtained will indicate the effectiveness of this technology at other sites. Treatment will be continued until results of soil bore leachate tests indicate that hydrocarbon removal efficiency has reached a plateau.

Status/Results: A venting program has been completed at one site; results showed that significant reduction of aromatic hydrocarbons can be expected. A former retail facility in Fullerton has been selected as the second site. The work plan has been approved by the project team and work has begun. Delays of over 5 months have occurred due to local permitting problems. A draft final report that includes the results from both sites is due in January 1991.

Completion Date: May 1991

FIELD TESTING OF VENTING PROCEDURES FOR CLEANUP OF UNDERGROUND HYDROCARBON CONTAMINATION -- 438

Objective: To develop and conduct a full-scale field test of venting techniques for the cleanup of subsurface hydrocarbon contamination.

Initiated: 1984

Scope: Promising results have been previously obtained using venting techniques to mitigate subsurface hydrocarbon contamination. In this study, the applicability of venting in a full-scale field application program was tested. Its emphasis was on the effective design and use of appropriate field equipment to promote a high level of product recovery. This was accomplished through optimizing various operating parameters, spacing venting wells, and varying the flow rates of the forced air ventilating system.

Status/Results: The experimental work is complete. Recovery of most of the volatile hydrocarbons was accomplished relatively quickly (days). A doubling of the evacuation rate did not materially improve the rate of recovery. A draft report is undergoing extensive evaluation and rewrite.

Completion Date: December 1990

MANUAL FOR DESIGNING SUBSURFACE VENTING SYSTEMS -- GW-4

Objective: To produce a reference document on the applicability of subsurface venting for the effective mitigation of vapors and recovery of products at spill sites.

Initiated: 1986

Scope: The contractor performed a critical review of available information on the design, operation, and maintenance of subsurface hydrocarbon venting systems, their application, cost-effectiveness, and limitations under a variety of site conditions. The effects of design and operating variables such as well spacing, soil types, evacuation rates, and materials selection on performance were examined.

Status/Results: A "how-to" manual containing detailed information on the technical aspects of subsurface venting has been submitted for review. The revised draft final report is being reviewed for editorial changes.

Completion Date: December 1990

SITE ASSESSMENT/DECISION TREE – GW-15

Objective: To develop a framework that facilitates cleanup decision-making at contaminated spill sites (soil and groundwater) based on an assessment of exposure and site considerations.

Initiated: 1988

Scope: The contractor will develop a three-component, computerized decision framework for evaluating the contamination potential of a subsurface release with respect to its down-gradient receptor (if any). The framework will offer assistance to the user in rapidly accessing information on key variables needed for input into the decision tree. The contractor is incorporating some of the variables, including hydrogeologic characteristics, chemical toxicity, persistence, transport, pathways, etc. The framework focuses on the importance of exposure consideration in deriving site-specific cleanup requirements. The end product will be a user-interactive software package based on the promulgated UST Final Rule on subsurface releases, as covered under various sections dealing with emergency response, health and safety requirements, site assessment, characterization, and cleanup. The framework will be especially useful in conducting negotiations with regulators at state and local levels on what, when, and how to carry out release management activities. Because of the flexibility inherent in the program, one can access data from a built-in database (information from API Publication No. 1628) and call in other stand-alone programs to perform additional tasks or calculations (there are several saturate and unsaturate models under development in other groundwater-related projects).

Status/Results: The project team and a consultant reviewed and provided comments on the Prototype 4 software. A new principal investigator has been named. The $15K amended funds will be used to add important technical information to the "screens" that software users can access. The revised software package will be "beta tested" by a preselected group of potential users (industry environmental managers and EPA UST Office and CHESS staff) who are unfamiliar with the program. The purpose of this effort is to uncover any "bugs" in the program code and to make refinements prior to release of the final software package.

Completion Date: March 1991

SOIL TREATMENT OF GASOLINE-CONTAMINATED GROUNDWATER BY SURFACE APPLICATION – GW-14A

Objective: To evaluate land application of contaminated groundwater containing soluble hydrocarbons as a potential treatment technology for gasoline spill sites.

Initiated: 1988

Scope: Field and laboratory studies will document the sorption, volatilization, and biodegradation of BTEX in water during steady-state infiltration after application to the soil surface. Data collected will be used to develop and validate a numerical model of these processes. This work is a follow-up to a previous field study that showed promising results (Removal of Soluble Petroleum Constituents through Soil Application Rehabilitation of Groundwater, API Publication No. 4475).

Status/Results: A site visit in February 1989 was held to finalize the work plan. Initial laboratory studies have been completed, and the modeling approaches have been worked out. Further laboratory studies are continuing. The field site has been instrumented and its hydraulic properties characterized. Additional field tests have been conducted and are continuing into the fall months. These studies compare the effects of different loading rates, BTEX concentrations, and water delivery methods. A draft final report of the laboratory, field, and modeling studies will be submitted by the end of November.

Completion Date: April 1991

TECHNOLOGY LIMIT AS ALTERNATIVE TO GROUNDWATER CLEANUP STANDARD – GW-11

Objective: To determine if statistical methods can determine from monitoring data the practical limit of the in-place remediation technology.

Initiated: 1987

Scope: Phase I -- The contractor performed a statistical evaluation of groundwater monitoring data from spill sites undergoing remediation. He evaluated two regression methods to determine if they are effective in identifying a limit beyond which further remediation by the in-place technology is impractical. Both of these methods will be made available on the API VAX system. In report form, the contractor will show the results of the evaluation, provide information on analytical limit of detection and site factors (e.g., natural attenuation) as added arguments for ceasing treatment, and address the apparent inflexibilities in current site-specific cleanup requirements.

Phase II -- As several states are adopting the asymptotic limit concept for assessing the effectiveness of ongoing cleanup programs for UST and are amenable to alternative cleanup goals on a site-specific basis, a stand-alone, PC-compatible software package will be developed. This package should offer more capability and flexibility than the one on the VAX system and will enable the industry to encourage wider dissemination of the concept and the tool to users and regulators.

Status/Results: Phase I -- The contractor has completed the statistical evaluation of the site monitoring data and analyzed some of the factors affecting variability and its impact on determining the asymptotic limit. He also evaluated both linear and nonlinear approaches and has data to show the relative effectiveness of each. The final report is being balloted.

Phase II -- The contractor has completed the first version of the program code. The beta test version will be delivered in October.

Completion Date: January 1991

U.S. Environmental Protection Agency (EPA), Groundwater R , D & D Initiatives

Clinton Hall, EPA
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Ada, Oklahoma

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THE CURRENT STATE-OF-THE-ART OF *IN SITU* BIOREMEDIATION: CONSIDERATIONS, LIMITATIONS, POTENTIAL AND FUTURE DIRECTIONS

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INTRODUCTION

Increasing costs of current treatment technologies, more stringent regulatory requirements, and a more favourable attitude in the regulatory agencies to examine innovative technologies have positioned bioremediation to play an important role in the treatment of hazardous wastes in the 1990s. Research into biodegradation of xenobiotic organic compounds has been ongoing for decades and a plethora of data and papers are available on the subject. What is being recognized is that this research can be applied to cleaning up contaminated soils and groundwaters.

The general premise of *in situ* bioremediation is to stimulate biological activity in soil or the subsurface to biodegrade contaminants. The underlying premise of *in situ* bioremediation is the Ubiquity Principal which states "...all types of bacteria are available at all times everywhere...". Hence, with the right selection pressure applied to the microbial populations it is possible to stimulate the required biological activity to degrade a contaminant. Stimulation of biological activity can be achieved by improving or modifying geochemical or physical conditions, or by adding nutrients or selected microorganisms.

Application of *in situ* bioremediation requires a thorough *understanding* of the microbiology. This understanding is achieved by having an information base on microbiology, biochemistry and genetics, understanding of the metabolic processes which lead to the degradation of the contaminants, and a comprehension of the structure and function of microbial communities. There is also a strong interaction between the microbial community in surface and subsurface soils and the physical and geochemical environment. Each influences the other, creating a dynamic environment in which contaminants are degraded.

PURPOSE AND OBJECTIVES OF THE STUDY

The purpose of this study is to undertake a review of the state of the art of *in situ* bioremediation. For the purposes of this study, the definition of *in situ* bioremediation was:

> The enhancement of biological activity in soils and/or groundwater by manipulation of the geochemical and/or environmental conditions, and/or addition of selected, adapted or engineered microorganisms or assemblages of

microorganisms, for the purpose of degrading and/or altering the contaminants *in place*.

This definition is important since many organizations call their bioremediation process *in situ* when it is fact on-site. The definition includes landfarming but not treatments requiring excavation of soil or pumping of groundwater to a treatment system. Excavation of soil and its slurrying and placement in a bioreactor, composting, or its placement in an engineered system is considered on-site bioremediation. Groundwater that is pumped to the surface *for treatment*, is considered on-site treatment. Groundwater pumped for the purpose of hydrogeological control, nutrient addition or pretreatment prior to its reinjection into the subsurface, such that biodegradation activity occurs *in place*, is considered part of *in situ* bioremediation. Bioremediation synonyms include, bioreclamation, biodegradation, biostimulation and biotreatment.

This review is composed of information obtained from "grey" literature (consultant and government reports, trade journals) and companies practising bioremediation. The three main objectives of this project were:

1) to describe current research and development status by identifying individuals and organizations involved on a national and international level, the type of research being conducted and the objectives of the research, progress to date, and expected outcome;
2) to identify and describe pilot and commercial application of *in situ* bioremediation in sufficient detail to allow replication or reproduction; and
3) to identify information gaps in bioremediation research in order to identify further research needs.

Study Approach. Scientific and trade literature, conference proceedings, computer searches and personal knowledge were used to develop an initial list of individuals and entities who are involved in bioremediation on a commercial and research level. Contacted individuals were asked if they were interested in responding to a questionnaire. This questionnaire was designed to obtain detailed information on the commercial application of *in situ* bioremediation and current research and development efforts. The same questionnaire was sent to both research and commercial institutions and was designed to obtain information of the range of options applied to bioremediating a contaminated site and what they felt was needed in terms of research efforts. The questionnaire information categories solicited and the rational is presented in Table 1.

We endeavoured to obtain the best information possible and provide a comprehensive evaluation. However, many commercial organizations were wary of providing detailed information to another consulting firm, and often provided only general information or promotional material. Other organizations were quite agitated about providing what may be proprietary or trade secret information that they had spent years developing. Letters of confidentiality did not allay those fears.

RESULTS

Response to Questionnaire. Over 60 organizations were initially identified and contacted to determine if they would be interested in participating in the study. For various reasons (work-load, only subcontract bioremediation companies, not involved in commercial application of bioremediation) some companies declined to respond after receiving the questionnaire. Other organizations were particularly concerned about releasing "trade secrets" and proprietary information to what could be a competing consulting firm. Some companies did not respond even after agreeing to participate in the study. Additional information on the activities of non-responsive or other organizations was obtained after a search of the grey literature.

TABLE 1: QUESTIONNAIRE INFORMATION AREAS

Information Solicited	Rationale
Matrices treated	Limitation
Monitoring/injection wells and delivery	Determine well construction, drilling protocols since use of drilling muds or water will affect the data quality (microbial and geochemical)
Control of groundwater and gases	Level of effort and strategies used to control groundwater and vapour movement.
Chemical/nutrient additions	Determine how and types of microbial activity stimulated.
Microbial information	Type and level of assessment; Types of microorganisms used.
Monitoring information	Assess the effectiveness of biodegradation and prove biodegradation is occurring.
Contaminant	Treatment efficacy and range of contaminants that can be treated
Site assessment	Determine site parameters used to evaluate if a site can or cannot be bioremediated and what the relationship is between these parameters for designing a bioremediation strategy.
Promotional and case history information	Case study.
Research and Development	Current research and research needs.

In all only 7 organizations responded. Their responses were combined with case histories and the overview is presented below. Over 60[1] case histories, supplied by the companies or obtained from the grey literature, were also reviewed to obtain information on how the technology is being applied. In particular, information was sought on;

- types and conditions of contaminated sites;
- general configuration (system design) of bioremediation ;
- nutrients and electron donors/acceptors added;
- how the microbial populations were assessed;

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[1] This includes the 8 laboratory, 8 pilot and field demonstrations, and 22-full scale applications provided by the Applied BioTreatment Association. A majority of the case studies (23 of 38) involved on-site versus *in situ* bioremediation. Additional sources of case histories are supplied in the bibliography

- duration and efficacy of bioremediation; and
- problems associated with applying the technology

Although the case histories of *in situ* bioremediation and organizations involved is not exhaustive we feel that it provides a good cross-section showing how bioremediation is currently applied and the directions in which it is moving.

Site Types and Contaminants Treated. The sites examined can be classified into one of three groups:

- gas/service stations, transfer lines
- marshalling yards, storage (transfer) facilities
- industrial facilities

The aerial extent of the contamination ranges from 90 to 25,000 square metres. There was no relationship between the type of contaminant and the aerial extent of contamination. The depth to the water table was typically 1-8 metres (maximum was 30 metres). The hydraulic conductivity of subsurface sediments ranged from 10^{-1} to 10^{-10} m/s. However, contamination at sites that had hydraulic conductivities of less than 10^{-6} m/s was generally limited to surface soils which could be bioremediated by landfarming strategies. Subsurface soils were generally sand/gravel mixtures with some clay interbeds. Several sites include highly fractured or channelled limestone bedrocks.

Table 2 presents a breakdown of the frequency of contaminants treated. Contaminants in the fuels/hydrocarbons category were the most commonly treated contaminant, followed in order by contaminant categories, aromatics, creosote/coal tar/PAH, and chlorinated aliphatics. The contaminant categories of chlorinated aromatics and alcohols/ketones/aldehydes (organic solvents) were treated at the same frequency.

Table 3.3:Frequency of Chemical Class Treated

Fuels/ Hydrocarbons (e.g. gasoline, diesel, Jet, kerosene, oil)	Creosote, Coal Tar, PAH	Aromatics (BTEX, phenol, nitrobenzene)	Chlorinate Aromatics (e.g. PCB, substituted benzenes and phenols)	Chlorinated Aliphatics (e.g. TCE, carbon tetrachloride, methylene chloride)	Alcohols Ketones and Aldehydes (e.g. methyl ethyl ketone, methanol)
19	5	6	2	4	2

Most fuels and hydrocarbons contamination originated from gasoline stations or underground storage tanks. Aromatic compounds are more soluble in water and are often used as fuels additives. Their higher solubilities and ubiquitous use contributes to their frequency as a commonly treated class of compounds. Creosote, coal tar and PAH are often associated with coal gasification plants, railway yards and wood treating facilities. The compounds in these three classes are also frequently treated for two reasons:

- familiarity with their biodegradation because of numerous laboratory and field studies; and
- microorganisms and consortia of microorganisms that aerobically degrade these compounds are commonly isolated from soil and groundwater and are easily manipulated in the laboratory.

Thus it is reasonable to predict that soil and groundwater contaminated with these compounds could be bioremediated.

The low frequency of treating organic solvents is not surprising. Alcohols, ketones and aldehydes are recognizable substrates, readily metabolized, and would be quickly removed from the environment. These contaminants would not likely persist in the environment after their release. Further, many of these compounds have higher water and soil standard criteria and lower human health risks.

Chlorinated compounds are infrequently treated. Those that are generally limited to low- chlorinated derivatives. For example, several companies claimed to successfully treat PCBs, but only the lower arochlors. The treatment involves the aerobic degradation of the lower arochlors and assumes that higher arochlors will be tightly bound to soil organic fraction (Major and Fitchko, 1990). Recent research has shown that this may not be suitable since higher arochlors can be dechlorinated to lower arochlors under anaerobic conditions.

Chlorinated aliphatics such as trichloroethene (TCE) and tetrachloroethene (PCE), have been treated in bioreactors. Ecova has isolated a Pseudomonas specie that degrades TCE aerobically while growing on toluene (Nelson *et al.*, 1986, 1987, 1988). TCE and PCE concentrations have decreased in a groundwater aquifer at the Kelly USAF Base during aerobic *in situ* bioremediation (Wetzel *et al.*, 1987) The loss of these compounds was suspected to be due to degradation in anaerobic zones (this was not confirmed). The application of *in situ* bioremediation for the treatment of TCE is being conducted by Stanford University at the Moffet Air Force Base in California (Simprini *et al.*, 1989, Roberts *et al.*, 1990). Researchers of this project are examining the co-metabolism of TCE by methane-oxidizing bacteria growing on methane. Beak Consultants is currently studying how an anaerobic microbial population is degrading PCE and TCE to ethene (Major *et al.*, 1991). Field and laboratory evidence suggest that PCE and its daughter products can be dechlorinated anaerobically in the presence of methanol and acetate. A pilot scale remediation is to be attempted in the summer of 1991.

Chlorinated organics, multi-ring cyclic hydrocarbons (greater than 4 rings), polyaromatics and their substituted derivatives are the least frequently treated contaminants. This is not because they have lower frequency of occurrence in soil and groundwater, but rather due to:

- less information on how they are biodegraded;
- less familiarity and understanding of anaerobic degradation (which is how most highly chlorinated compounds are initially attacked);
- cometabolic and/or anaerobic strategies may need to be employed; and
- consortia of organisms are usually responsible for the degradation (synergism), thus making it impossible to isolate a single microorganism capable of utilizing the compound as a sole source of energy and carbon.

System Design/Configuration. A typical system configuration involves centrally withdrawing groundwater from the contaminated area and treating it in above-ground units to remove any contaminants. Treatment units used include air-stripping, activated carbon, physicochemical treatment and bioreactors. Once treated, the groundwater is aerated and nutrients are added. Treated groundwater is recirculated, using infiltration galleries and/or injection wells to form a closed loop. Infiltration galleries are often situated above the zone of contamination, so that the recirculated groundwater passes over residual contaminants bound to the soils in the vadose zone or floating on top of the water table. Injection wells are used to recirculate treated groundwater. They are also used for purging and batch addition of nutrients. Injection wells are often severally located at the periphery of the contaminated zone, so that the treated groundwater, nutrients, and/or electron acceptors move through the contaminated zone to the withdrawal well(s).

Treatment of the vadose zone can be achieved by raising the water table by deep well injection. This brings oxygen-enriched groundwater and nutrients in contact with residual contaminants. Alternatively, soil venting can be used to enhance biodegradation in the vadose zone (Hinchee *et al.*, 1989; Downey and Elliot, 1989; Ely and Heffer, 1988). Soil venting has the advantages of increasing the mass of oxygen that can be delivered to the hydrocarbons because of greater diffusivity and diffusion of gases. Soil venting strategies include:

1) drawing air through the centre of the contaminant mass by a centrally located vent well;
2) both injected and withdrawing air from the contaminant zone;
3) injecting air into the contaminant zone and withdrawing it from clean soils; and
4) injecting air into the contaminant zone but not withdrawing it (diffusion control to surface).

The choice of a strategy will depend upon the level of hydrocarbon off-gases produced. Strategy (1) minimizes pumping but probably maximizes off-gases and does not treat the capillary fringe. Strategy (2) may increase the amount of air coming in contact with the hydrocarbons. Strategy (3) is probably the best strategy since it allows some of the off-gases to degrade in the clean soil prior to withdrawal (i.e. minimizes off-gases). Strategy (4) does not control off-gases but may be appropriate for some sites. Soil venting can be combined with nutrient and moisture addition to enhance the rate of degradation.

The application of soil venting for bioremediation requires:

- optimizing air flow rates to minimize volatilization but maintain aerobic conditions;
- monitoring localized soil gas composition (not just vent gas composition) to ensure aerobic conditions are prevalent in the contaminant zone;
- adding nutrients and moisture to maintain or enhance biodegradation; and
- manipulating the water table for air/contaminant contact.

A variation of soil venting is *in situ* vacuum extraction combined with *in situ* and air stripping. This research is being conducted at the Savannah Research Laboratories in conjunction with the University of Tennessee (Jack Corey, pers. comm[2]). The purpose of this research is to evaluate the application of horizontal screened wells for the purpose of *in situ* air stripping and *in situ* bioremediation. One horizontal well is placed below the water table (ca. 50 metres below ground surface) and is used to deliver nutrients and gases. A second horizontal well (ca. 20 metres below ground surface) is placed in the vadose zone to capture the off-gas and any removed VOCs. Field trials of this project are scheduled for the summer of 1990. Further research is needed on how air flow in the saturated zone affects hydraulic conductivities and groundwater movement.

Landfarming techniques are used at sites where the contamination is limited to the surface and the chance for contaminants leaching to the groundwater is low. Landfarming typically involves daily tilling of the soil to increase aeration and periodic addition of limiting nutrients.

Microorganisms are rarely added because of the difficulties ensuring their distribution to the contaminants in the soil and/or groundwater. In cases where microorganisms have been added, the sources of the inoculum were rehydrated commercial preparations, secondary sludge from municipal facilities, on-site bioreactors or microorganisms selected and cultured from the site. Application of microbial inoculants has generally been limited to landfarming operations. The efficacy of microbial inoculants is also in question. Little or no data is provided on how effective the added microorganisms were compared to the stimulated indigenous species. Survival and activity data was not provided on the introduced species in the cases reviewed.

Electron Acceptors/Donors and Nutrients. The electron acceptor of choice for commercial application of bioremediation is oxygen. There are five methods for supplying oxygen to soil and groundwater (Brown *et al.* 1989; Michelson *et al.*, 1985, 1988):

1) Air sparging: Air or pure oxygen is supplied to the groundwater through porous-stone, sintered metal or sintered glass diffusers located at the bottom of the well.
2) Injection of aerated/oxygenated water: Withdrawn groundwater or water from another source is saturated with oxygen, then injected into the aquifer or through an infiltration gallery.
3) Venting: Air can be passed through the vadose zone either by injection or withdrawal. Vacuum withdrawal is often used for vadose zone treatment and has the advantage of removing volatile organic compounds.
4) Hydrogen peroxide addition: Hydrogen peroxide is added to water and reinjected. The hydrogen peroxide decomposes to oxygen and water.
5) Colloidal gas apherons: Encapsulation of air in 25-50 μm surfactant bubbles which can be dispersed into sand.

Oxygen solubility is often deemed to be limiting aerobic biological activity. Hydrogen peroxide added to water will decompose into oxygen and water. The decomposition of hydrogen peroxide allows the attainment of higher dissolved oxygen (D.O.) levels in groundwater (typically 40 mg/L), and a greater mass of oxygen to be delivered to the microorganisms, *in situ*, than sparging the groundwater with air. D.O. levels in sparged groundwater are typically 8-12 mg/L (Lee *et al.*, 1987). However, rapid decomposition of hydrogen peroxide can occur near the injection well because of peroxidase activity of microorganisms or reaction with iron, reducing the D.O. concentrations (Spain *et al.*, 1989). Hydrogen peroxide is usually added incremental up to 2000 mg/l. The incremental addition is to allow the microorganisms to acclimate to high concentrations of hydrogen peroxide.

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[2] Dr. Jack Corey, Technology Transfer, Westinghouse, Savannah River Laboratory, Aiken, CS. 29808.

Colloidal gas apherons have also been used to deliver oxygen to microorganisms in sand. Colloidal gas apherons are produced by bubbling air through surfactants which encapsulate the air in 25-50 μm bubbles. The bubbles are then pumped through the pore spaces of the sand to the contaminated region. This allows the intimated contact between the contaminate and air (Michelson *et al.*, 1985,1987).

There is a direct relationship between the mass of oxygen required and the mass of the contaminant (assuming that molecular oxygen is the only oxidant). The oxygen mass transfer rate is influenced by the delivery method. Oxygen delivery by air sparging relies on the flow of groundwater, which is dependent on the hydraulic gradient and hydraulic conductivity. The amount of oxygen supplied by water injection is a function of the injection rate. Similarly, oxygen supplied by venting is a function of the air flow rate. Oxygen supplied by hydrogen peroxide is both a function of the concentration of hydrogen peroxide and of the injection or infiltration rate into the groundwater.

The use of anaerobic processes to bioremediate contaminated sites is a possibility that has fostered a great deal of interest. The reasons for this interest include:

- release of organic compounds will often stimulate microbial activity and result in the formation of anaerobic areas within the contaminant zone or plume;
- some organic compounds may not degrade under aerobic conditions but will under anaerobic conditions (e.g. chlorinated hydrocarbons); and
- anaerobic electron acceptors are far more soluble in water than oxygen, thus it is easier to deliver them to the contaminated zones.

Anaerobic activities being examined include denitrification (nitrate or nitrite to nitrogen gas), sulphate reduction (sulphate to hydrogen sulphide) and methanogenisis (carbon dioxide to methane).

Nitrate addition is gaining some acceptance as an alternate electron acceptor. Nitrate or nitrite can be added to oxygenated water and promotes denitrification in anaerobic contaminant zones. However, nitrate does not serve as a source of oxygen for the degradation of organics as some organizations have claimed. Different enzymes and catabolic activities are induced under denitrifying conditions, and it is these activities and enzymes that degrade organic compounds.

Batterman and Werner (1984) were the first to document the field use of nitrate to clean up an oil spill in the upper Rhine catchment. Their treatment required the recirculation of the groundwater through a supply tank and pressure filter. The groundwater was sprayed into the tank to strip methane and dissolved gases (which would also remove some of the volatiles). Treated groundwater was then amended with nitrate, ammonia and ortho-phosphate and reinjected into the aquifer. The treatment over 300 days was judged successful, removing 16.6 tonnes (approximately 75%) of total hydrocarbon from the pore volume of the sand and consuming 50 tonnes of nitrate.

In general, the use of alternate electron acceptors has been limited to research sites and laboratory studies (Berry-Spark and Barker, 1987; Britton, 1989, Major *et al.*, 1990). University of Waterloo researchers (Berry-Spark *et al.*, 1988) have conducted several field experiments at Canadian Forces Base Borden. These experiments involved the injection of 2,500 L of groundwater spiked with benzene, toluene, ethyl benzene and xylenes (total BTEX of 0.9 mg/L) into a shallow sand aquifer to create two distinct BTEX plumes. Four days after this injection, additional groundwater was injected up-gradient of these plumes. Behind one plume, groundwater containing 45 mg/L of nitrate and 2,000 mg/L NaCl was injected. Non-amended groundwater was injected behind the second plume as a control. The results indicated that a remedial solution of nitrate could overtake, overlap and mix with the BTEX plume by the processes of advection and dispersion without requiring hydraulic controls such as pumping. There was an enhancement of toluene and m-xylene removal in the remediated plume.

Interestingly, no case studies documented the concept of coupling aerobic with anaerobic processes to degrade mixed wastes or recalcitrant compounds. This approach could be used to attack compounds such as PCE by first creating an anaerobic zone to promote dechlorination, followed by aerobic zones that would allow the degradation of the less chlorinated products that tend to persist in anaerobic zones but can be degraded aerobically.

Cometabolic strategies are still at a research or demonstration stage. The best known case is the field study conducted by Stanford University researchers at the Moffett U.S. Air Force base in California (Semprini *et al.*, 1988) The study is examining the induction of the methanotrophic bacteria (oxidize methane) monooxygenase enzyme to oxidize trichloroethenes. This process involves adding both oxygen (6 mg/L) and propanes/methane (3-4 mg/L) to water and reinjecting it into the aquifer. Their research has shown:

- methanotrophic bacteria can be stimulated in an aquifer which had not shown any previous methanotrophic activity;
- methane oxidation ceases when oxygen is removed, but resumes quickly after re-introduction of oxygen;
- mass balance of oxidants/reductants and contaminants; and
- methanotrophs can be stimulated to degrade TCE, DCE isomers and VC.

In general, a decrease in the degree and rate of degradation was observed with increased number of chlorine atoms on the ethene molecule. The process has not been shown to effective for chlorinated ethanes. Stanford is in the process of applying for a patent for this process. This process could be coupled with soil venting strategies.

Nutrients are often added to groundwater and soil to stimulate microbial activity. Typically, nitrogen and/or phosphorous are determined to be limiting and are added as inorganic salts (e.g., ammonium chloride, ammonium nitrate sodium nitrate, sodium and potassium phosphate) to achieve concentration in the groundwater of 1 to 100 ppm of nitrogen and/or phosphorous. Soil venting processes have delivered nitrogen as ammonium gas. Some nutrients, particularly phosphorous, precipitate out in groundwater as insoluble salts leading to a reduction of available nutrients (reduction of biologically activity) and clogging of the aquifer. Iron, manganese and magnesium are added as trace nutrients (10-100 ppb) usually in the form of chloride or sulphate salts.

Other compounds that have been added include buffers (e.g. NaOH) to neutralize pH, and dispersants and emulsifiers (e.g. Corexit 7664) to increase the available surface area of the contaminants to the microorganisms.

Microbial Assessment. Little microbial analysis is provided in the case studies (the emphasis is usually on the hydrogeology and a few gross parameters of soil and groundwater geochemistry). The microorganisms typically enumerated are total heterotrophs (i.e. microorganisms that use carbon compounds as their energy and carbon source), hydrocarbon- and gasoline-utilizing bacteria. The enumeration of these microbes is usually limited to analysis of groundwater by plate counts techniques. This approach has two major drawbacks:

- introduction of culturing bias; and
- the microbial ecology between groundwater and soil is significantly different.

Culturing of selected microbial groups can provide misleading information on the activity, composition and biomass of surface and subsurface soils. For example, enumeration of hydrocarbon-degrading bacteria only provides information on the presence of the bacteria, not on their activity or non-activity. This is particularly true of enumeration of microorganisms from unsaturated zone sediments. David White and Tom Phelps (per. comm.) compared the estimation of biomass by plate count and phospholipid fatty acid analysis of various sand/clay mixtures, under saturated and unsaturated conditions (>20% clay; > 70% sand, unsaturated; >70% sand, saturated). The two measures were in close agreement for saturated soil samples with more than 20% clay or a sand content greater than 70%. However, the plate count over-estimated the active biomass in the unsaturated sand sample. Further, plate counts had a standard deviation of over an order of magnitude between replicate soils (n=10). The standard deviation of lipid analysis was considerably lower (half an order of magnitude). Caution should be exercised in the interpretation of biomass increase during bioremediation. The increase could be due to sample variation.

Over-estimation can also occur when enumerating heavily contaminated soils and/or groundwater. Table 3 compares microbial activities of microorganisms with depth and TCE concentration. The activity was not measured by the number of microorganisms but by incorporation of [^{14}C]acetate into lipids and [^{14}C]thymidine into DNA. At high TCE concentrations DNA synthesis is turned off (zero incorporation of thymidine). At higher concentrations, acetate is still incorporated into the lipids (lipid turn-over), indicating that the microbes are active but not necessarily growing (no DNA synthesis). At even higher concentrations both acetate and thymidine incorporation stops, indicating inhibition of cell activity. Areas below and above the most heavily contaminated zones show biological activity. Culturing methods would likely remove the inhibition of TCE and allow the cells to start to grow. This could result in the conclusion that cells were active in the heavily contaminated zone.

The use of media to culture the biomass can also underestimate the active biomass since it can repress the growth of microorganisms most notably the oligotrophic organisms. Oligotrophic microorganisms survive and grow at low organic substrate

TABLE 3: ACTIVITIES OF MICROORGANISMS FROM SEDIMENTS CONTAMINATED WITH TRICHLOROETHENE[1]

Depth (m)	[^{14}C]Acetate Incorporation into Lipids (dpm)[2]	[^{3}H]Thymidine Incorporation into DNA (dpm)[3]	Trichloroethene Concentration (ug/kg soil)
3	147	1700	-
	820	0	-
10	7600	0	-
	180	1900	-
	660	12000	670
20	680	4200	320
	2000	11000	190
	13000	0	250
30	130000	0	16000
	0	0	310000
	0	0	42000
	0	0	59000
40	0	0	361000
	0	0	373000
	290	0	38000
50	82	0	-
	170000	74000	-
	30000	1100	-
60	210000	36000	-
	2200	3800	-
	130	0	-
	53000	0	-
70	2300	1600	-
	250	2100	-
75	0	2000	-

concentrations and are suppressed or die at higher concentrations. Oligotrophic and other specially adapted microbes can play an important part in biodegradation since they are adapted to scavenge very low concentrations of organic compounds. This ability is important to harness when trying to achieve drinking water standards. Oligotrophic microorganisms cannot be enumerated using conventional plating or enumeration techniques. The media utilized tends to be high, relatively speaking, in organic carbon and is more appropriately applied to enumerate eutrophic microbes (i.e. those that grow and survive at high organic substrate concentrations). Thus, the initial assessment of the site may indicate a low number of requisite microbes (i.e., eutrophic microorganisms are not dominant). As the bioremediation proceeds the eutrophic microbes may begin to grow and multiply resulting in higher plate counts. However, the total active biomass has not changed, only shifted to microbes that will grow under the culturing conditions. The higher plate count, therefore, does not indicate that the contaminants are being degraded by the eutrophic microbes, but that conditions have changed to allow them to grow.

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[1] Data from Phelps *et al.* (1989)

[2] Incorporation of [^{14}C]acetate into lipids expressed as dpm/day determined from duplicate time course experiments

[3] Incorporation of [^{3}H]thymidine into macromolecules expressed as above.

Research conducted by Rice University at the USAF Traverse City addressed the problem of enumerating oligotrophic gasoline-utilizing bacteria by using a noble agar/mineral salts medium exposed to gasoline vapours (Ward *et al.*, 1988). This agar medium is free of organic compounds and allows the growth of oligotrophic microorganisms.

The use of other monitoring techniques (lipid analysis, DNA probes, incorporation of precursors) should be used in conjunction with classical (culturing) methods to better understand the indigenous microbial population. These alternate techniques eliminate the bias of culturing and provide a snapshot of the microbial population pre-, during, and post-treatment. These techniques can also be coupled with tracers (stable and radiolabelled) to show which subsets of the microbial populations are active and/or utilizing the contaminants. Culturing techniques are more appropriate for determining if selected physiological groups or species of microorganisms can be induced to grow under existing or modified geochemical and environmental conditions.

Isolation and identification of various microorganisms is occasionally documented, but is not highly relevant. The use of lipid biomarkers or DNA-probes are useful for tracking both indigenous and released microbes in soil matrices. Knowing how the target microbes are distributed, their level of activity, and their role in degrading contaminants is far more useful than knowing which specific microorganisms are present. Similarly, the case studies do not document the survival, fate and activity of released microorganisms. Thus the efficacy of their release cannot be evaluated.

The use of DNA-probes and lipid analysis to evaluate the microbial population biomass and its degradation activity was demonstrated by the University of Tennessee and Oak Ridge National Laboratories (Donaldson *et al.*, 1988). The field experiments involved evaluating PCB bioremediation in field lysimeters. DNA-probes (which were specific to DNA sequences that code for the catabolic enzymes responsible for PCB degradation) and lipid analysis (for microbes known to degrade PCB) were used to assess both indigenous and inoculated PCB-degrading microorganisms in soil. Both the DNA-probes and lipid analysis correlated positively with PCB degradation and the presence of PCB-degrading microorganisms.

A laboratory evaluation is required for assessing biodegradation potential and capabilities of microorganisms in soils and groundwater. This is usually accomplished by placing soil and/or groundwater in contained vessels, modifying the conditions and monitoring biodegradation (i.e. microcosms). The contained environments are called microcosms. Key to the use of microcosms is the attainment of realistic condition of the environment. Details of laboratory biodegradation tests are usually lacking, but when they are supplied they indicate that the treatment conditions used for assessing biodegradation of contaminants does not adequately reflect real-world environmental conditions (e.g. incubation temperature is elevated, use of groundwater and not soil/groundwater mixtures, continuous shaking). The use of microcosms that reflect as much as possible the site conditions is essential. Unrealistic testing conditions can lead to extreme over-estimation of biodegradation rates and produce artificial data on what microorganisms or groups of microorganisms are involved in the degradation.

The problems with the laboratory testing is further compounded by the lack of quality assurance and quality control associated with the collection of representative soil and groundwater samples. Except for research sites, little attempt is made to ensure that the soil and groundwater samples are not being contaminated by surface microorganisms and drilling muds. Laboratory tests conducted with samples contaminated with surface microorganisms will lead to false conclusions on subsurface microbial activity, population composition, nutritional status and biodegradation capabilities.

The development of *in situ* testing devices (Gillham *et al.*, 1990) allows field experiments to determine the effect of various treatments on bioremediation and field controls under natural field conditions. These devices also allow "sterile" experiments to be conducted in the field. The main advantage of these devices is that they have been demonstrated to provide similiar data as obtained with more expensive natural-gradient field injection experiments. However, the observed degradation patterns in these devices were different than degradation patterns observed in parallel microcosm experiments (Acton, 1990). This futher emphasises the problems of extrapolating biodegradation laboratory data to the field.

Duration and Efficacy. The efficacy of bioremediation is difficult to determine by comparing various case studies because of the various levels of contamination, and cleanup and evaluation criteria utilized at each site. The cleanup times (of the bioremediation phase of cleanup) ranged between 2 months and 3 years. Sites contaminated with gasoline and fuel hydrocarbons were the fastest to cleanup; aqueous hydrocarbon concentrations typically were reduced 2-3 orders of magnitude. Aqueous concentrations of chlorinated hydrocarbons were reduced by 30-50% depending on the contaminant. Efficacy of the process was usually determined by:

- decrease in contaminant concentration in groundwater (rarely in soils);
- increase in total heterotrophic, "gasoline" or hydrocarbon" utilizing microorganisms;
- consumption of oxygen and nutrients; and
- production of CO_2 (in the case of soil venting).

These evaluation criteria and endpoints make it difficult to evaluate bioremediation case studies. This problem is compounded by the reliance of groundwater versus soil samples for organic contaminant analysis. The Elgin USAF base case study showed that aqueous concentrations of aromatic hydrocarbons had decreased significantly (from 8 ppm to <200 ppb), but there was no measurable decrease in total petroleum hydrocarbons concentration in soil samples. Wilson *et al.* (1989) stressed the inadequacy of well water analysis to describe total hydrocarbon contamination. This deficiency prevents reasonable evaluation of nutrient and electron acceptor mass balance needs for bioremediation. Most of case histories emphasized the hydrogeology, geology and engineering. There is usually little or insufficient microbial data. Table 4 is a list of criteria that should be used to evaluate bioremediation claims.

Not all of the criteria can be expected to be met. Adaptation/acclimation response may not be evident at old contaminated sites since the microbial population may have

TABLE 4: CONFIRMATION OF BIODEGRADATION CLAIMS

- Mass balance between contaminants, nutrients and end-products
- Increase in biomass and activity of requisite microorganisms
- Production of expected end-products and/or intermediates
- Consumption of electron donor/acceptors
- Adaptation/acclimation response
- Biodegradation kinetics
- Field controls

already adapted. Intermediates or end-product may not accumulate since they may be quickly utilized by other microbes. However, the carbon flow should be examined to ensure that no undesirable DOC is created and not being accounted. This could be done by using stable and radio isotopes to trace the carbon, hydrogen, and oxygen flow.

Mandatory criteria should include mass balance between the contaminants, nutrients and end-products, increase in biomass and activity of biodegrading microorganisms, consumption of electron donors/acceptors, biodegradation kinetics and field controls.

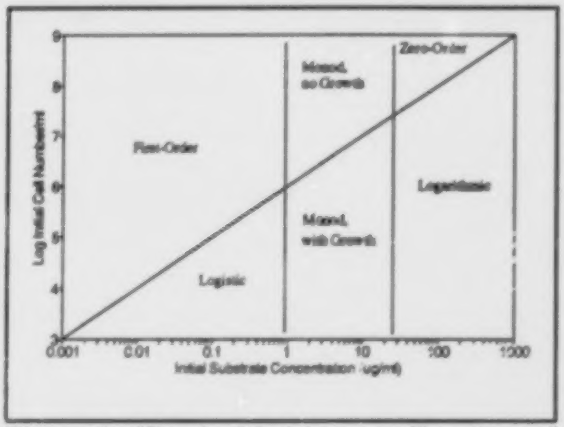

Figure 1: Kinetic Models as a Function of Substrate Concentration and Bacterial Cell Density (Alexander, 1985).

Of these criteria, mass balance determinations will be the most difficult to determine accurately. Various factors will affect the mass balance determination and accuracy. Generally, contaminant mass that exists only as a dissolved or vapour phase can be more accurately estimated (within half an order of magnitude). Contaminants present in soils and groundwaters as free-phase or residual liquids will increase the uncertainty of estimating the mass (1 - 2 orders of magnitude). The degree of monitoring will also increase or decrease the accuracy of the estimate. A spill scenario is the only case where the mass of the contaminants could be accurately known. The fraction of organic carbon of the soil and the presence of other natural labile organic compounds also affect the mass balance determinations since these compounds will degrade into other organic and inorganic degradation products. Since these reactions will also consume electron acceptors, it is important to analyze the soil and groundwater for additional labile organic compounds.

Determination of biodegradation kinetics requires information on the initial population densities of specific or physiological groups of microorganisms that will be responsible for contaminant biodegradation. Further information will be needed on how the contaminates are degraded (i.e. as a carbon and energy source, co-metabolism, secondary-substrate utilization). With this information it is possible to predict *a priori* the kinetics of growth and mass loss. Figure 1 shows how initial microbial population densities and substrate affect growth mass loss kinetics.

Field controls are lacking in many case studies (research studies are the exception). A minimum level of field control would be the comparison between treated and untreated areas. Additional controls could include a comparison between two plots to compare the effect of water addition (or circulating groundwater) with and without addition of nutrients. This type of control is thought to be necessary since disturbance effects can stimulate microbial activity or help mobilize available nutrients.

Problems. The most common problems encountered during *in situ* bioremediation include:

- clogging of screens and infiltration galleries with fines and microbial growth;
- maintenance of stable oxygen concentrations over time and throughout the contaminated zone;
- fluctuations in the water table causing a release in bound hydrocarbons;
- production of bioemulsifying agents which mobilize bound contaminants leading to an apparent increase in the concentration of contaminants in groundwater samples;
- clay units which act as sinks for hydrocarbons and thus become long-term sources;
- precipitation reactions (particularly phosphorous) which remove added nutrients and lead to clogging;
- rapid decomposition of hydrogen peroxide resulting in poor oxygen distribution; and
- fuel residuals in the vadose zone occluded in pores making them inaccessible to passing water and hence nutrients and oxygen.

FUTURE RESEARCH NEEDS

Microbial ecology and biogeochemistry of contaminated sites. Understanding the microbial ecology of contaminated sites will lead to better predictions of the efficacy of *in situ* bioremediation. The various roles of microorganisms in different microbial communities (aerobic, anaerobic) in degrading various contaminants, particularly halogenated compounds, needs to be clarified. This involves a better understanding of the physiology and metabolism of each microbial member (or group) playing a role in the biodegradation process. It also includes a better understanding of the competition of the various members for available resources, and the role of oligotrophic microorganisms. Insight into these areas will also provide a basis for understanding how microbial communities develop which can or cannot degrade contaminants.

A better understanding of microbial ecology of unsaturated areas is required to advance biotreatment. The impact of oxygen content, nutrients, soil moisture and type, and contaminants on microbial ecology needs to be explored.

It is critical to gain a better understanding of fundamental principals of microbial ecology and contaminant biodegradation. Coupled with the interplay of geochemical and physical factors, it will lead to a better prediction of the application of bioremediation. The frequently heard statement that bioremediation is site-specific, underscores more our lack of understanding of contaminant microbiology and microbial ecology than the fact that each site is unique.

Development of monitoring techniques. The microbial community needs to better evaluated, monitored and assessed. Monitoring and assessment techniques need to be developed that can be used *in situ* or on representative samples to evaluate the microbial population (total, individual species and physiological groups) in terms of activity, nutritional status (starved, not starved), biomass, composition, distribution and biodegradation capabilities. The techniques are required so bioremediation can be validated and the bioremediation process adjusted and monitored during treatment.

The development and application of monitoring techniques and tools is critical to advancing *in situ* bioremediation. These tools and technique enable us to collect better information which can be added to a database. Over time this information can be used to identify key parameters and relationships that can be used to assess a site and predict the outcome.

Laboratory assessment. Laboratory protocols and criteria for the assessment of biodegradation potential need to be improved. This includes development of standards for sample collection and handling, microcosm design, concentration effects, and controls. Standardized methods would aid in providing a yardstick for comparison of different sites and would ensure that common principals are used to interpret the results of laboratory evaluations.

Increase in scope of application. Bioremediation could be more broadly applied in terms of range of contaminants treated and treatment of low permeability zones. It would entail broadening treatment strategies such as use of alternate electron acceptors and donors, cometabolism, secondary-substrate utilization, analog addition, use of emulsifying agents. The application of sequenced redox zones needs to be explored.

Introduction of microorganisms. Addition of isolated and selected naturally-occurring microbes with novel degradation capabilities will, together with genetic engineering, play an increasing role in bioremediating sites. The conditions employed in the laboratory to assess biodegradation potential are not usually the conditions encountered in the open environment. Thus there is a need to understand how introduced microorganisms can survive, grow and degrade contaminants under sub-optimal conditions. This may require development of special introduction techniques or additives that will ensure both that their survival is long enough to accomplish the task and that they are distributed well enough to reach the contaminants in the system.

Delivery of nutrients and electron acceptors. Many contaminants degrade optimally under aerobic conditions. However, the availability of oxygen is limited in most cases. There is a need to increase stability and distribution of various electron acceptors, notably hydrogen peroxide. Use of high oxidative force potential for delivering gas (e.g. O_3) as a phase should be explored.

Further studies are required on gas transport in the vadose zone to understand factors which would affect the design of air delivery systems for enhanced biodegradation by soil venting.

The role of geochemical and sorption reactions on the availability of nutrients for microorganism uptake needs to be defined. This information will help in designing delivery systems and formulation of nutrients for application under various geochemical and redox conditions.

Models. Current mathematical models of *in situ* bioremediation are based on solute transport models which have been modified to include a biodegradation reactive term (Rafai *et al.*, 1988). Biodegradation is assumed to be instantaneous with respect to groundwater flow. Growth and hydrocarbon and oxygen utilization are assumed to follow a modified Monod function, and simple stoichiometric relationships to exist between total hydrocarbons and oxygen consumption.

These types of models are useful to predict the concentration distribution of reactants within the aquifer. However, they do not provide information on:

- changes in the biomass in terms of specific species or functional groups, their associated activities, and catabolic capabilities;
- changes in the geochemistry due to microbial activity and how this may influence the activity of the microbes; and
- impact of other competing reactions, end-products or labile organics.

More dynamic models are required which could help validate field results as well as test different treatment scenarios, designs and operating policies. There is a real need to develop models that incorporate anaerobic and cometabolic processes.

CONCLUSIONS

In situ bioremediation, as currently practised, has been limited to simple hydrocarbon contamination and typically entails the addition of an oxygen source and nitrogen and phosphorous to the contaminated matrix. The major limitation to advancing the predictability and efficacy of the technology is a better understanding of the response and involvement of the microbial community during *in situ* bioremediation. Information on changes to the microbial population has been lacking. A database on microbial responses would help identify key microbial parameters and correlations that could be measured prior to attempting *in situ* bioremediation.

The advancement of the technology is further curtailed because of little integration between the disciplines of microbiology and hydrogeology. This is evident by the studies are dominated by one or the other disciplines.

There is a need to standardize approaches and criteria for assessment of *in situ* bioremediation *a priori*, during and post treatment. The lack of standards makes it difficult to currently evaluate the *in situ* bioremediation claims.

As currently practised, the state-of-the-art of *in situ* bioremediation is not state-of-the-art. This is in part due to slow transfer of research results from the university to the commercial sector. However, key to developing this technology from an art to a predictable and effective technology requires better understanding of fundamental processes and the development of monitoring techniques and tools.

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IN-SITU INTERCEDENT BIOLOGICAL BARRIERS FOR THE CONTAINMENT AND REMEDIATION OF CONTAMINATED GROUNDWATER

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INTRODUCTION

Biofilms occur in many natural and artificial aquatic systems including groundwater. Microbial attachment to surfaces, liquid-liquid, and air-liquid interfaces constitutes a natural strategy by the microorganisms to optimize available nutrients for population growth (Fletcher et al, 1980; Costerton et al, 1987). Surfaces and interfaces are principal sites for the accumulation of nutrients due to adsorption or deposition. Attachment or association with surfaces is fundamental to cell and tissue microbiology since many microbial and tissue cells cannot divide unless associated with surfaces (Pethica, 1980).

Biofilms are beneficial in wastewater treatment systems such as trickling filters, where the high reactive surface areas allow for the uptake and degradation of the substrates present (Characklis, 1973, 1981). McCarty et al (1984) indicate that, owing to the ecological advantages of sessile bacterial populations in substrate utilization, biofilms in aquifer systems constitute the most important biological component for biodegradation of contaminants.

More frequently, biofilms constitute a nuisance, since prolific growth leads to biofouling. In cooling towers, heat exchangers and pipeline systems biofouling reduces efficiency (Characklis, 1981), and colonies of sulphate reducing bacteria can cause metal corrosion and system failure. In groundwater, biofouling results in the effective plugging of well screens and porous media by dense interlocking microbial slimes and associated biogenic metal deposits (Cullimore and McCann, 1977; Van Beek and Van der Kooij, 1982; Smith and Tuovinen, 1985; Cullimore, 1990a). Biofouling of water wells and media can result in up to 95% reductions in flow. Frankenberger et al (1979) have stated that the hydraulic conductivity of soils can be substantially reduced by bacteria, presumably in biofilms. Burns (1980) and Paul and Clark (1988) state that microbial adhesion is fundamental to the aggregation of soil particles.

A second issue to consider is that the decomposition of organic contaminants in surface water, groundwater, and soils can be linked to groups of bacteria associated with biofouling. Pseudomonads, in particular, are known to colonize petroleum hydrocarbon-water interfaces (Fletcher et al, 1980; Pethica, 1980; Rosenberg et al, 1980), bitumen surfaces (Costerton, 1983), and can utilize substrates like quinoline from oil shale (Shukla, 1986). Eagon (1983) stated that pseudomonads are capable of utilizing hydrocarbons as substrates and this will account for the proliferation of this genera in petroleum hydrocarbon plumes in groundwater (Lee et al, 1988).

The above issues are of interest since biofouling could be exploited as a physical containment strategy, and as a means of transforming a part of an aquifer into a fixed film bioreactor for the removal or degradation of organic contaminants. This dual application is illustrated schematically in Figure 1. Figure 1a represents a containment scenario using the native geological material as the host matrix for the bio-barrier. This type of situation could work well for permeable granular materials that offer relative textural and structural homogeneity. However, heterogeneity with respect to the media structure or textures, or low permeability media (e.g. clay, silt and fine sand, glacial tills and so on) could impact on the ability to develop a consistently structured bio-barrier. The alternative in these cases is represented in Figure 1b whereby the target area is excavated and backfilled with a sorted and coarse granular material. Starr and Cherry (1990) presented a proposal that high permeability barriers could be effective for contaminant containment. Here, the objective is to use the coarse medium as a homogeneous host matrix for a bio-barrier.

The purpose of this paper is to describe and discuss baseline experiments that have been undertaken to demonstrate that biofouling of porous media can be achieved simply by manipulating the nutrient supply, and secondly, to examine the efficacy of the resulting primary (young) and mature biofilms in removing phenol, benzene, toluene, xylene (BTX), and gasoline as contaminants.

APPROACH AND METHODS

The experimental program consisted of three microcosm configurations. Two of the systems were essentially the same differing only in the physical dimensions of columns used (e.g. 0.05 m by 0.50 m versus 0.10 m by 3.00 m). The discussion will concentrate on the smaller systems that were subject to biofouling, microbial and organic chemical analysis. The third configuration used involved established and matured biofilms (2 year old) in sealed model well systems. In this case, the primary goal was to assess the removal of high concentrations of gasoline by the established biofilms, and to eliminate complications caused by volatilization and liquid phase separation in continuous recycle experiments.

Forty-two column experiments were run using 0.05 m dia by 0.50 m long clear polycarbonate columns as depicted in Figure 2. The packed column serves as the host for the biofilms. Preliminary experiments (6 columns) were run with 0.5 cm dia gravel (crystalline quartz, feldspar and so on). The bulk of the experiments (36 columns) was operated with 20-30 mesh Ottawa silica sand. A second head column was added to allow for natural gradient flow, and to allow for the monitoring of flow during the plugging process. All feed lines were Tygon tubing with 0.15 m long silicone segments in pump heads. A 10 channel peristaltic pump was used to recirculate groundwater from 11 L polyethylene feed tanks.

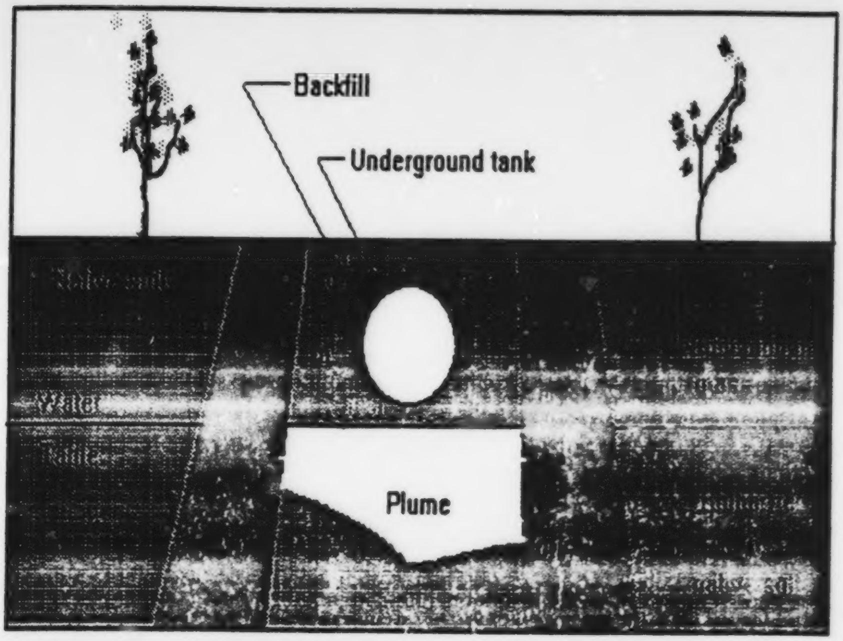
Backfill
Underground tank
Plume

FIGURE 1a - BIOBARRIER IN NATIVE SOIL MATERIAL

The native geological material serves as the host matrix for the biological barrier. Nutrients are injected or introduced passived to the target zone.

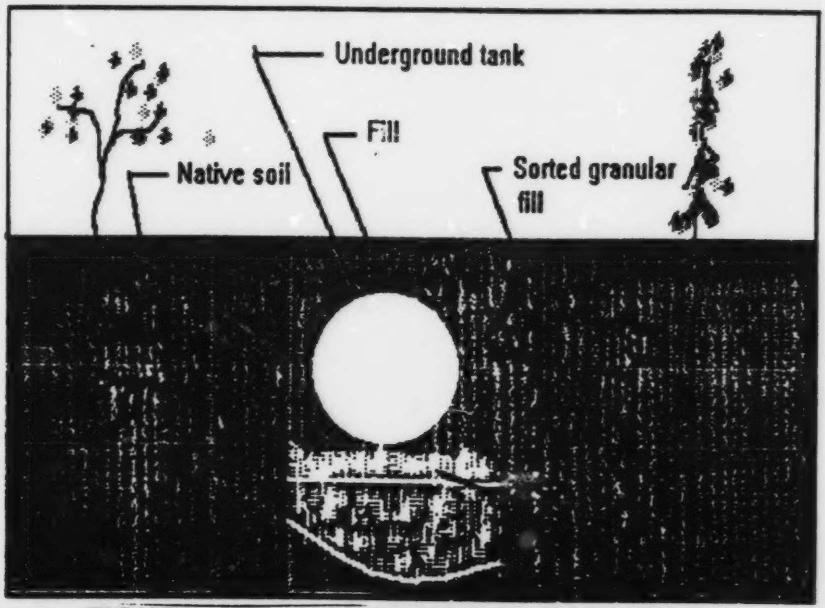
Underground tank
Fill
Native soil
Sorted granular fill

FIGURE 1b - BIOBARRIER IN SORTED FILL

For fine textured, low permeability material, or for heterogeneous media, a trench is excavated around the contaminated zone, and replaced by sorted granular material to serve as the host matrix

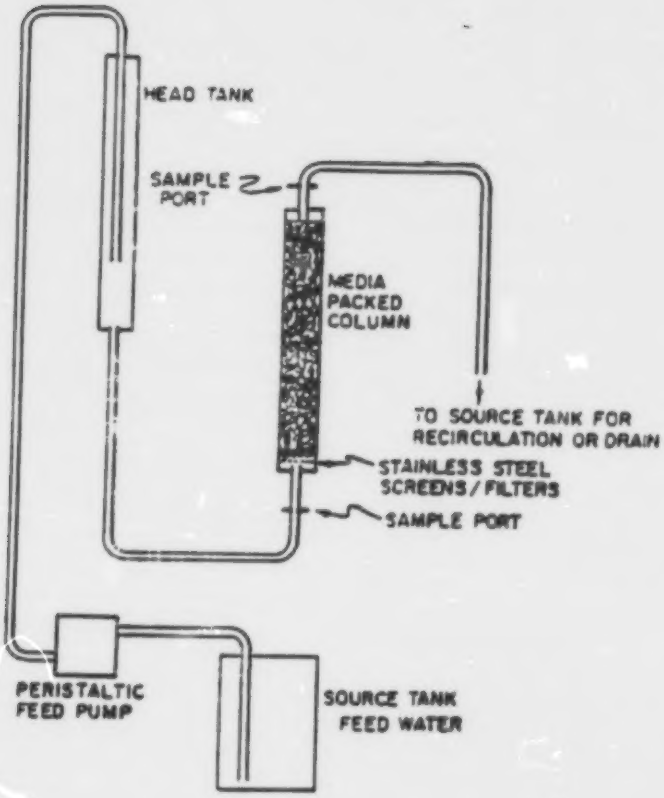
HEAD TANK
SAMPLE PORT
MEDIA PACKED COLUMN
TO SOURCE TANK FOR RECIRCULATION OR DRAIN
STAINLESS STEEL SCREENS / FILTERS
SAMPLE PORT
PERISTALTIC FEED PUMP
SOURCE TANK FEED WATER

FIGURE 2 - SCHEMATIC SHOWING THE EXPERIMENTAL COLUMN SET UP USED FOR SAND AND GRAVEL MEDIA

The decision was made to use a synthetic groundwater made up from laboratory distilled and deionized water, that, owing to storage in large reservoirs and unsterilized piping systems, has an indigenous bacterial population of about 4 x 10^4 cfu/mL. Reagent grade mineral salts were added to the water in the proportions shown in Table 1. This gives a groundwater chemical profile similar to that shown by Matthess (1982, p 224). The laboratory water provided a consistent and continuously available source, in contrast to local groundwater supplies that may have considerable chemical variability on a temporal basis.

TABLE 1

Synthetic groundwater was formulated using a distilled deionized laboratory water supply and mineral salt enrichments shown below. Concentrations shown are in mg/L

Potassium nitrate	1.8
Ferrous chloride	0.9
Magnesium sulphate	0.9
Calcium carbonate	73.0
Magnesium carbonate	7.3
Sodium carbonate	13.0
Calcium chloride	4.5

Biofouling of the microcosms was achieved by manipulating the carbon:nitrogen:phosphorus ratio (160:8:1) and by increasing the nutrient loadings to the systems. Reagent grade urea, ferric citrate (FC), ferric ammonium citrate (FAC), and dipotassium hydrogen orthophosphate were the only major nutrients used.

Reagent grade phenol, benzene, toluene, and xylene (BTX) and a commercial gasoline were used as contaminant substrates. The BTX additions were in the ratio of 2:1.5:1 to approximate concentrations present in a gasoline. Therefore, the loadings of 17.5 mg/L would correspond to about 100 mg/L of gasoline. Phenol in preliminary experiments was determined by a portable colorimetric test kit. Due to variability and potential error in the measurements, the data obtained represent the mean of three samples. BTX was determined by direct GC-FID analysis. Gasoline was determined by spectrophotometric methods.

Twelve of the 40 columns were sacrificed for microbiological analysis. The media was extruded from the columns and analysed for 4 quadrants (5.0 cm and 17.0 cm from the influent, and 17.0 cm and 5.0 cm from the column effluent ends; henceforth referred to as quad 1, 2, 3 and 4 respectively). Three successive elutions using sterile Ringers solution and agitation detached the biofilms. The first elution as a rinse removed the detachable fraction; the second elution with 2 minutes manual agitation sheared the second fraction;

and a third elution with 5 minutes of violent vorticular agitation was used to remove the tightly attached fraction. The total biofilm volume removed from each quadrant sample (10 g) was based on the elutions. A laser driven particle counter was used to determine the population density. Bacterial loadings to the biofilms were computed as a sum of the bacteria present for each quadrant. Spread plate counts and cultures were used to enumerate the bacterial populations as to genus and, where possible, to species with the aid of a computer driven microbial identification system.

RESULTS AND DISCUSSION

Biofilms and biofilm growth are dependent on a number of environmental factors including pH, temperature, oxygen and/or availability of electron acceptors such as NO_3, SO_4, dissolved organic carbon, nutrient availability (nitrogen and phosphorus salts), and electrolyte composition (Characklis, 1973, 1981; Marshall, 1980). In field situations, the induction of biofouling will be dependent on those factors that can be readily manipulated. In this case, the pH and the temperature cannot be effectively controlled. As has been suggested by Cullimore (1990a), while pH can influence initial attachment events, once biofilms are established the exopolymeric matrix and the biomass create a microenvironment that satisfies ecological needs and is independent of the external environment. Temperatures will vary with depth, seasonally, and, possibly, on an event specific basis. In temperate regions, water temperatures in the subsurface can vary from 1 to 25°C, and cannot be effectively manipulated. Although temperature will impact on metabolic functions, with decreased activity at lower temperatures, biofouling can still occur, based on available field evidence. The electrolyte concentrations can also impact on initial biofilm growth events. Marshall et al (1971) have shown divalent cations such as Ca and Mg appear to increase attachment events, while trivalent cations can impede attachment, presumably because the bacteria have to compete for sorption or ion exchange sites. Manipulating the electrolyte concentrations may be possible. However, interaction between the solid matrix and the aqueous environment will invariably define the ionic composition of the environment. The value and efficacy of altering the electrolyte chemistry of the groundwater is, therefore, not known.

Oxygen is a growth limiting factor. A number of authors have indicated the provision of dissolved oxygen and/or the availability of electron acceptors may be critical in establishing biofilms and in promoting the biodegradation of organic contaminants. However, it is our opinion that air sparging, or the introduction of an oxidizer like hydrogen peroxide is not necessary as an amendment. It will be shown subsequently that, as the biofilms mature, the environment within the biofouled zone will shift from aerobic to strongly anoxic conditions based on the decline in dissolved oxygen. The point, here, is that once biofouling is initiated, oxygen enrichment may not have a significant impact on subsequent maturation of the biofilms.

The factor that should influence biofilm growth and consequent biofouling is the availability of an accessible carbon substrate, plus nitrogen and phosphorus. Groundwater environments are frequently deficient in organic carbon and nutrients which accounts for the low populations and oligotrophic conditions encountered in many aquifers (Bone and Balkwill, 1988). Although severe oligotrophic conditions can inhibit a growth response by nutrient enrichment, the fact that biofouling can occur in aquifers indicates that a portion of the population is responsive to carbon and nitrogen plus phosphorus enrichment. Therefore, the experimental program has limited the environmental manipulation to these three parameters.

The goal, here, is to show that simple nutrient enrichment can cause biofouling, at least in an experimental microcosm. Cullimore and McCann (1977) have indicated that iron bacteria are adapted to the use of citrate as a carbon source. It was hoped that, by adding citrate along with iron (FC, FAC), plugging by iron bacteria would be induced. Lee et al (1988) have indicated that bacteria in groundwater are adapted to the use of citrate, acetate, glucose and other sugars, proteins and hydrocarbons. The challenge is to provide a carbon substrate at a concentration that will facilitate biofilm growth, and, secondly, to provide nitrogen and phosphorus as nutrients. In high carbon environments, biofilms will be thick, have a low shear strength, and will have low population densities (Characklis, 1981). Conversely, low carbon environments will feature tight, low volume and densely populated biofilms that are resistant to shearing. It is well known that soil microbes will not mineralize organic carbon when the carbon:nitrogen (C:N) ratio exceeds about 20:1 (Stevenson, 1982). The population immobilizes all available nitrogen simply to meet metabolic requirements. Wardell et al (1980) indicated that the bacteria in biofilms will excrete or synthesize exopolymeric matter, and, as Cullimore (1990b) has noted, the bacteria within the biofilms will focus on cell metabolism. Excess carbon traumatizes the bacteria. Population growth and biofilm expansion will occur if the carbon loading is balanced by an appropriate nitrogen and phosphorus loading. Cullimore (1990b) has indicated that phosphorus can be a limiting nutrient in groundwater environments and that an optimal N:P ratio falls in the range of 4 to 8:1.

Since biofouling is to be applied as a containment and remediation strategy for contaminated groundwater, the objective is to provide a sufficient loading of carbon, nitrogen and phosphorus in the ratio of 160:8:1.

BIOFILM GROWTH

Initial microbial attachment can be spontaneous. However, most authors argue that surface conditioning precedes cell attachment. In this case, due to surface charge, nutrients, cations and polysaccharides are sorbed onto the surfaces (ZoBell, 1943; Marshall et al, 1971; Fletcher and Floodgate, 1973; Fletcher, 1980; Marshall, 1980). The process of surface conditioning, followed by cell deposition and attachment, is very rapid. Also, once biofilm development has been induced, the exopolymeric matrix plus biomass undergoes a metamorphosis from a gelatinous reversibly attached mass to a densely populated, interlocking and fibrous mat that is irreversibly attached to the surface. Once this state has been achieved, removal of the biofilms is extremely difficult.

Characklis (1981) and others have identified three phases of biofilm growth in linear systems. These are:

(a) initial log-phase growth of rapid biofilm expansion until the surface becomes saturated by biofilms and the exopolymeric matrix reduces the mass transfer of substrate and nutrients;

(b) linear phase growth dominated by slow biofilm growth, due to the mass transfer limitations imposed by the biofilms;

(c) at some critical thickness, dictated by the hydraulic conditions of the environment, a plateau or equilibrium phase is reached whereby new biofilm additions are balanced by sloughing at outer surfaces.

For gravel media experiments, at least four phases of growth have been identified from replicated columns. These phases have been identified primarily from the flow data, as is shown in Figure 3. Visual observations during initial biofilm growth was facilitated by the clear columns. The first phase of growth is indicated by the rapid decline in the flowrate to about 30% of the initial. From observations, initial attachment events or induction include: discrete colonies visible due to iron pigmentation; biofilm coalescence; rapid expansion with a stratified structure - a densely populated inner layer at the media surface, and a gelatinous translucent outer layer. The second phase is marked by biofilm contraction (possibly due to metamorphosis to a dense fibrous mat), or to shearing of the outer polymeric material due to limited shear resistance. The third phase is dominated by slow biofilm expansion, and periodic pulsations that have been attributed to local plugging which, in turn, reduces the supply of nutrients and substrate and induces lysis followed by shearing. The fourth plateau phase is indicated by the sustained minimum flowrate obtained. Based on the dissolved oxygen profile shown in Figure 4, it is clear that, as the biofilms mature and plugging occurs, a shift from aerobic to anoxic conditions also occurs. Adding oxygen by bubbling air in the feed tanks had no detectable impact on the dissolved oxygen concentrations in the effluent lines from the columns.

The addition of phenol to the gravel systems at concentrations up to 140 mg/L had no apparent impact on initial biofilm induction. Clear indications of inhibition were obtained at 500 mg/L, and no signs of biofilms were apparent with initial shock loads > 1,000 mg/L. Phenol is a known antiseptic, and the inhibitory effects are most likely due to phenol toxicity.

For the sand media experiments, flowrate data show marginal decreases with apparent pulsations in early stages of growth. Plugging occurs as a rapid and almost instantaneous event. The plugging of the sand occurred in as little

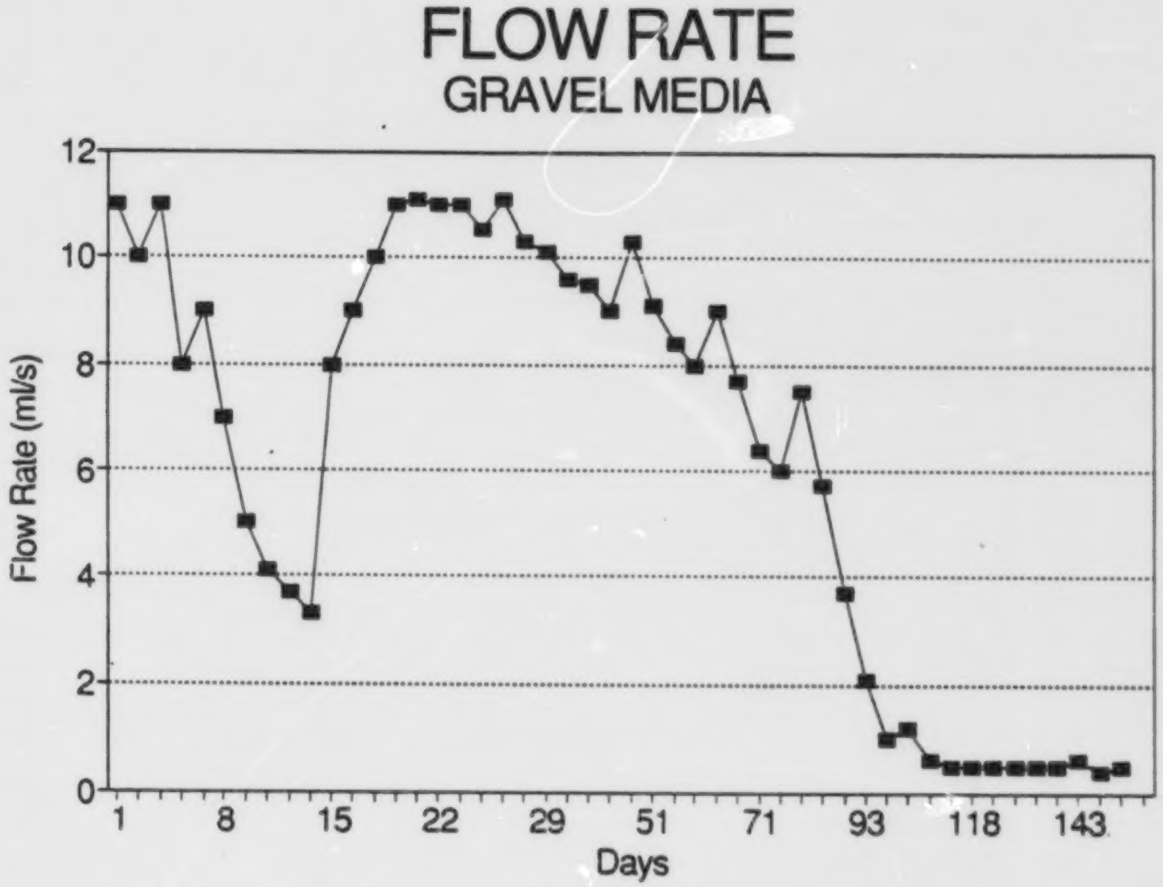

FIGURE 3 - TIME SERIES PLOT OF FLOWRATES IN GRAVEL MEDIA

Four phases of growth are indicated. (1) Rapid biofilm growth resulting in flow reduction over the first 10 days; (2) biofilm contraction or sloughing with a corresponding rise in flowrates to initial levels; (3) gradual biofilm growth with pulsating flow and ultimately a 95% reduction in flow in the plateau phase (4)

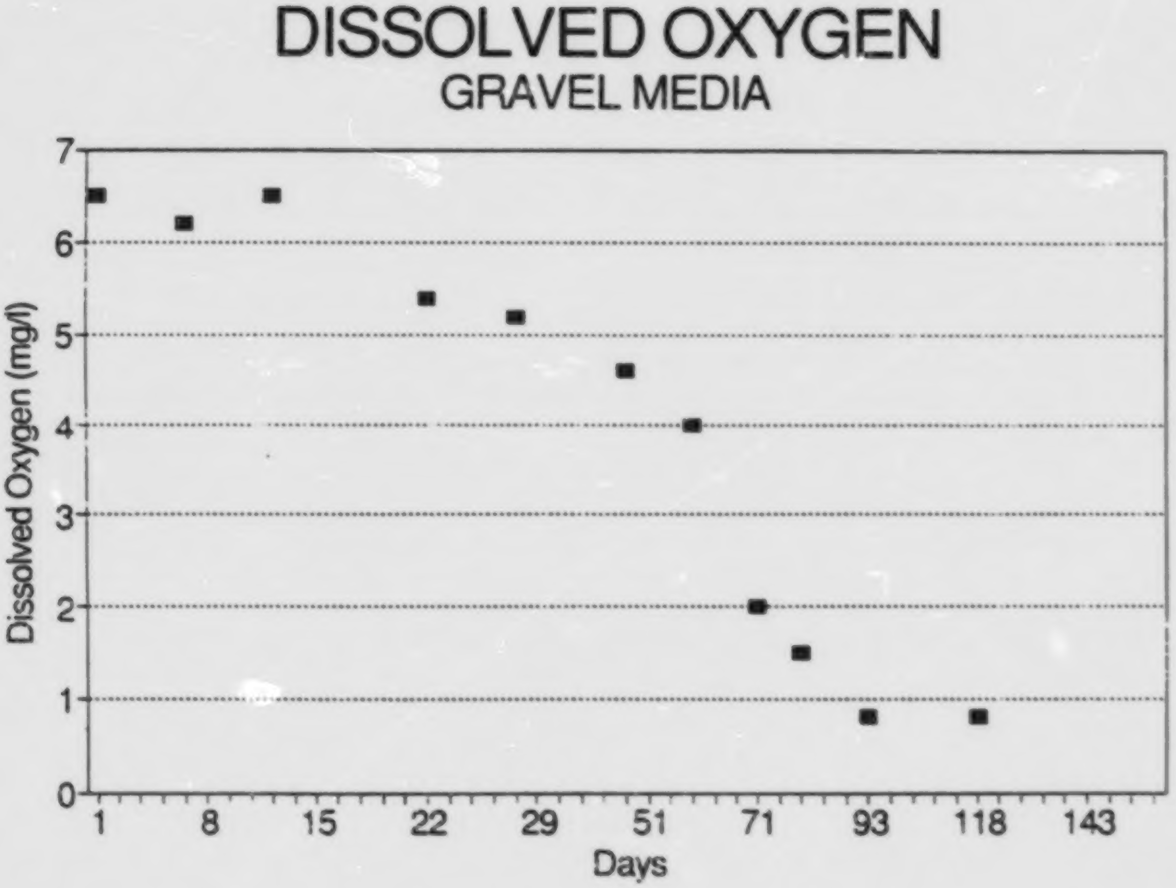

FIGURE 4 - DISSOLVED OXYGEN CONCENTRATIONS IN GRAVEL MEDIA

As indicated, the dissolved oxygen levels declined as the biofilms matured. The final concentrations reached a minimum value of 0.8 mg/L as 3 days and no inhibitory effects appeared for BTX loadings ranging from 17.5 mg/L total BTX, to 500 mg/L total BTX. Plugging in one column receiving 280 mg/L BTX occurred in 3 days versus an unspiked control that was plugged in 18 days.

Having established that biofilms and biofouling can be induced in porous media, the next issue is whether or not the biofilms and biobarriers are persistent. Experimental microcosms have been maintained in a biofouled state with a basic groundwater supply for periods in excess of 2 years. Evidence from field cases involving biofouled water wells shows that, once established, biofilms are highly resistant to removal. Costerton (1983) has noted that biocidal agents have a limited effect on the established biofilms, due to the effective barrier presented by the exopolymeric matrix. Once attachment and growth of biofilms have occurred, reversal of the process is difficult.

MICROBIOLOGICAL ASSESSMENT

The microbiological analysis has focussed on basic attributes of the biofilm structure and integrity that can be defined by the biofilm volume, population density, bacterial loadings to the biofilms and the genera/species of the bacteria in the biofilms. As indicated, only 12 of the 40 columns have been assessed. Specific comparisons between individual columns cannot be made since they are derived from different experiment sets. As well, the individual experimental cases represented received varying concentrations of BTX. This will impact on the within- and between-column data variability. Table 2 is a legend for the experimental conditions for each of the 12 columns represented in the analysis.

Biofilm Volumes

The biofilm volume data are shown in Figure 5. For each column, a histogram was constructed for each column of the influent and effluent quadrants (e.g. 5.0 cm (quad 1), 17.0 cm (quad 2) from influent, 178.0 cm (quad 3), 5.0 cm (quad 4) from effluent). The biofilm volume has a finite maximum value determined by the pore spaces. Superficially, the unplugged and unenriched columns (1, 2, 3, 7, 8) have similar biofilm volumes to those from the plugged and enriched columns (4, 5, 6, 10, 11, 12). Column 9 exhibits an anomalously high biofilm volume in quad 1 and has been attributed to the trapping of biomass and suspended solids between the influent cap and the sand.

Population Density

The density of encumbency of bacteria within the sand columns are shown in Figure 6. In this case, the population densities are demonstrably higher in the plugged versus unplugged columns. This trend would reflect a growth response to the carbon, nitrogen and phosphorus loadings. Carbon is

TABLE 2 - Experimental Conditions (Legend) for the 12 Columns Sacrified for Microbiological Analysis

These represent replications from the total set of 40 columns run using Ottawa sand as the porous medium

FAC - Ferric ammonium citrate
FC - Ferric citrate
DHO - Dipotassium Hydrogen Orthophosphate

Column	Conditions		
1	Synthetic Groundwater	(Col 2, exp2)	
2	Synthetic Groundwater	(Col 2, exp 3)	
3	Municipal Tap Water	(Col 1, exp 3)	
4	Synthetic Groundwater	(Col 3, exp 3)	17.5 mg/L Total BTX 197 mg/L FAC 960 mg/L FC 9 mg/L DHO
5	Synthetic Groundwater	(Col 4, exp 3)	35 mg/L Total BTX 197 mg/L FAC 960 mg/L FC 9 mg/L DHO
6	Synthetic Groundwater	(Col 5, exp 2)	35 mg/L Total BTX 45 mg/L FAC 1640 mg/L FC 45 mg/L Urea 17 mg/L DHO
7	Municipal Tap Water	(Col 1, exp 2)	35 mg/L Total BTX
8	Synthetic Groundwater	(Col 3, exp 4)	35 mg/L Total BTX 197 mg/L FAC 960 mg/L FAC 9 mg/L DHO
9	Synthetic Groundwater	(Col 3, exp 5)	35 mg/L Total BTX 197 mg/L FAC 960 mg/L FC 9 mg/L DHO
10	Synthetic Groundwater	(Col 6, exp 3)	140 mg/L Total BTX 197 mg/L FAC 960 mg/L FC 9 mg/L DHO
11	Synthetic Groundwater	(Col 4, exp 5)	70 mg/L Total BTX 197 mg/L FAC 960 mg/L FC 9 mg/L DHO
12	Synthetic Groundwater	(Col 5, exp 5)	140 mg/L Total BTX 197 mg/L FAC 960 mg/L FC 9 mg/L DHO

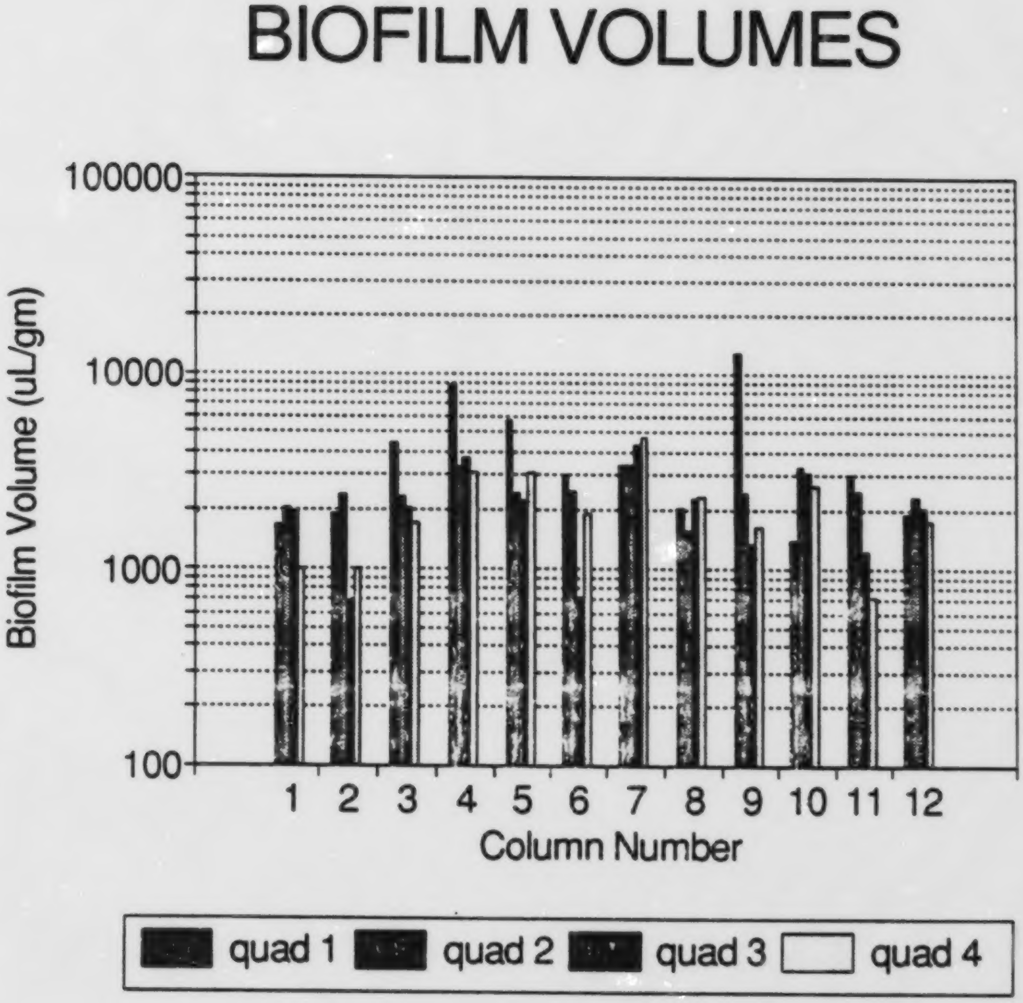

FIGURE 5 - HISTOGRAM PLOT OF BIOFILM VOLUME DATA FOR EACH QUADRANT OF 12 COLUMNS DISSECTED

Quad 1 corresponds to the influent, while Quad 4 corresponds to the effluent. The data show considerable variability within each column, although comparison of sample means using a Student's t test on grouped, plugged columns 4, 5, 6, 10, 11, 12, and unplugged columns 1, 2, 3, 7, 8 show different populations. Column 9 shows an anomalous influent biofilm volume that is due to the trapping of biomass and suspended solids

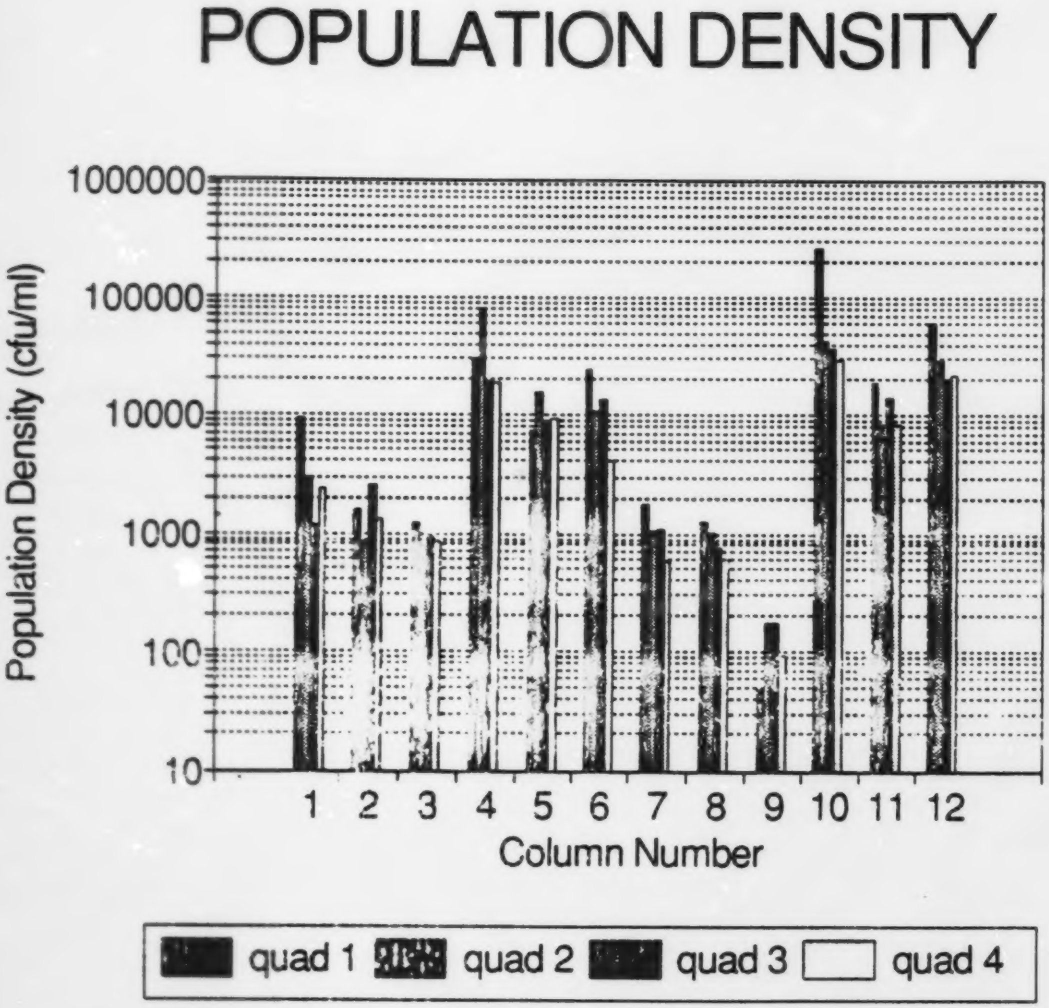

FIGURE 6 - POPULATION DENSITIES IN THE 12 DISSECTED COLUMNS

The plugged columns show substantially higher population densities when compared to the unfouled sets important. Marshall et al (1971) have indicated, excess nitrogen will not contribute to population growth unless carbon is available. Therefore, without the addition of a carbon source,the addition of N and P alone will not induce plugging.

Bacterial Loadings

The bacterial loadings are presented in Figure 7 and are derived from the sum of bacteria present in each quadrant and summation for the column total. Although there is considerable variability between the individual columns, the plugged columns show substantially higher bacterial loadings.

Bacterial Enumeration

The bacterial populations have been enumerated for gross aerobes as an index of response to the nutrient additions; pseudomonas as a potential hydrocarbon degrader and response indicator; and iron related bacteria that should respond to the FC or FAC enrichment. In general, the gross aerobe data, as presented in Figure 8, vary, with indications of higher populations associated with quad 1 and 2 locations, and with nutrient enrichment. This indicates that the populations have responded favourably to nutrient addition. In spite of the FC and FAC additions to the columns, the iron bacteria have not shown a consistent response to the nutrients added to the columns, as indicated in Figure 9. Figure 10 shows the pattern for the pseudomonad populations. The data indicate higher populations are encountered in the columns that received nutrients and which became plugged (e.g. columns 4, 5, 6, 10, 11, 12).

Statistically, the microbiological data on biofilm volumes and population densities indicate differences between the plugged and unplugged columns. Based on ANOVA (one-way) methods, the variance within the individual columns is significantly greater than between the columns, both for the biofilm volume and population density (calculated $F = 0.68$ (biofilm volume), and $F = 0.75$ (population density), versus a tabled value $F = 2.05$ for 11 and 36 degrees of freedom). A Student's test on the grouped data for the plugged and unplugged columns indicates that there are significant differences in means for the two groups. This shows that the sample populations and column conditions differ for the two groups. This difference is illustrated by the plotting of population density and biofilm volume, as in Figure 11. As shown, the data for the plugged columns are clustered separately from the unplugged cases. The principal difference is the significantly higher population densities relative to biofilm volume in the plugged columns. Biofouling or plugging in these cases would be associated with relatively high populations, and relatively lower volumes of exopolymeric matter and a dense interlocking mat to account for the resistance to flow. The lack of nutrients and/or contaminant loadings should contribute to weak, exopolymer abundant biofilms. No consistent pattern is evident that the highest BTX concentrations used have inhibited or altered the biofouling process. The issue here may be a function of massive abiotic losses

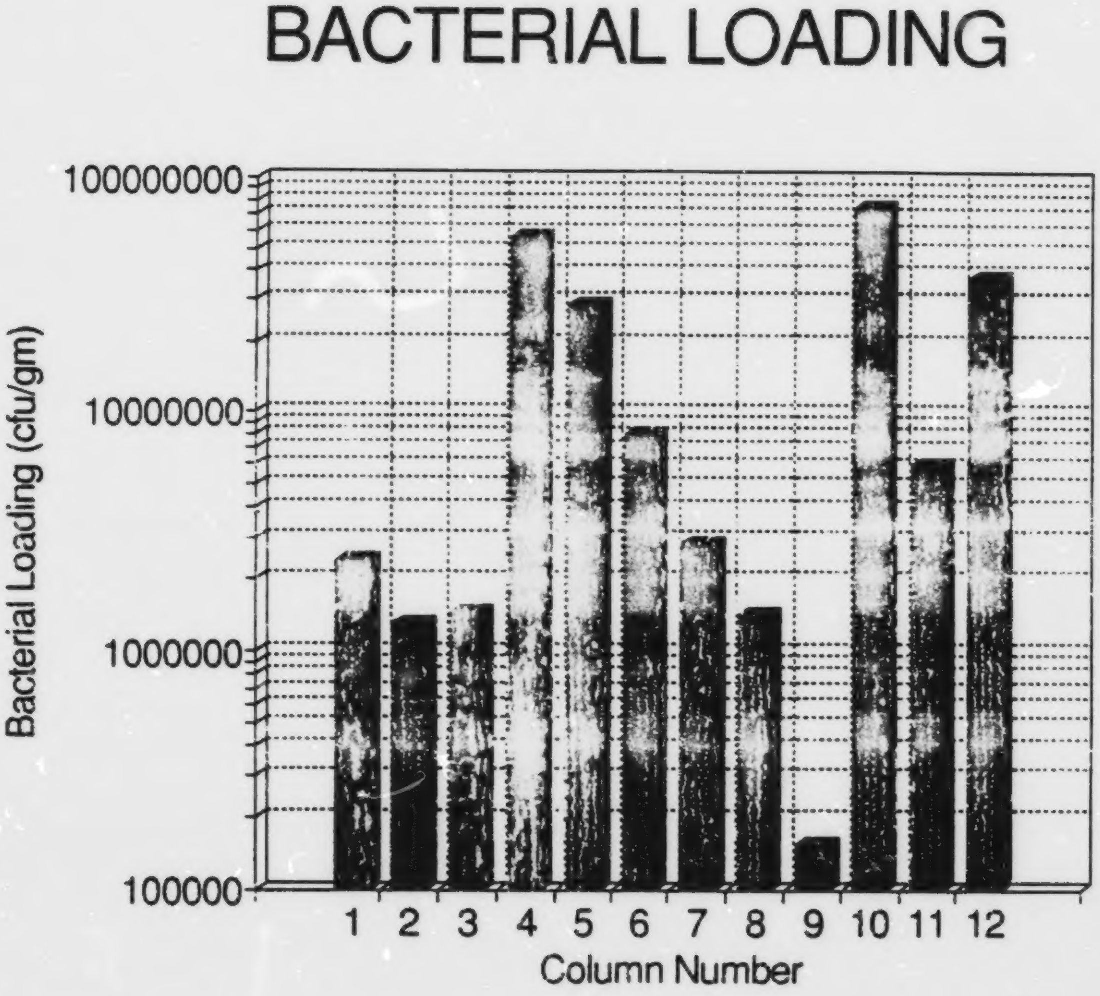

FIGURE 7 - BACTERIAL LOADINGS

The bacterial loadings as a sum of incumbent bacteria present in each quadrant and column shows higher loadings in the plugged and nutrient enriched columns

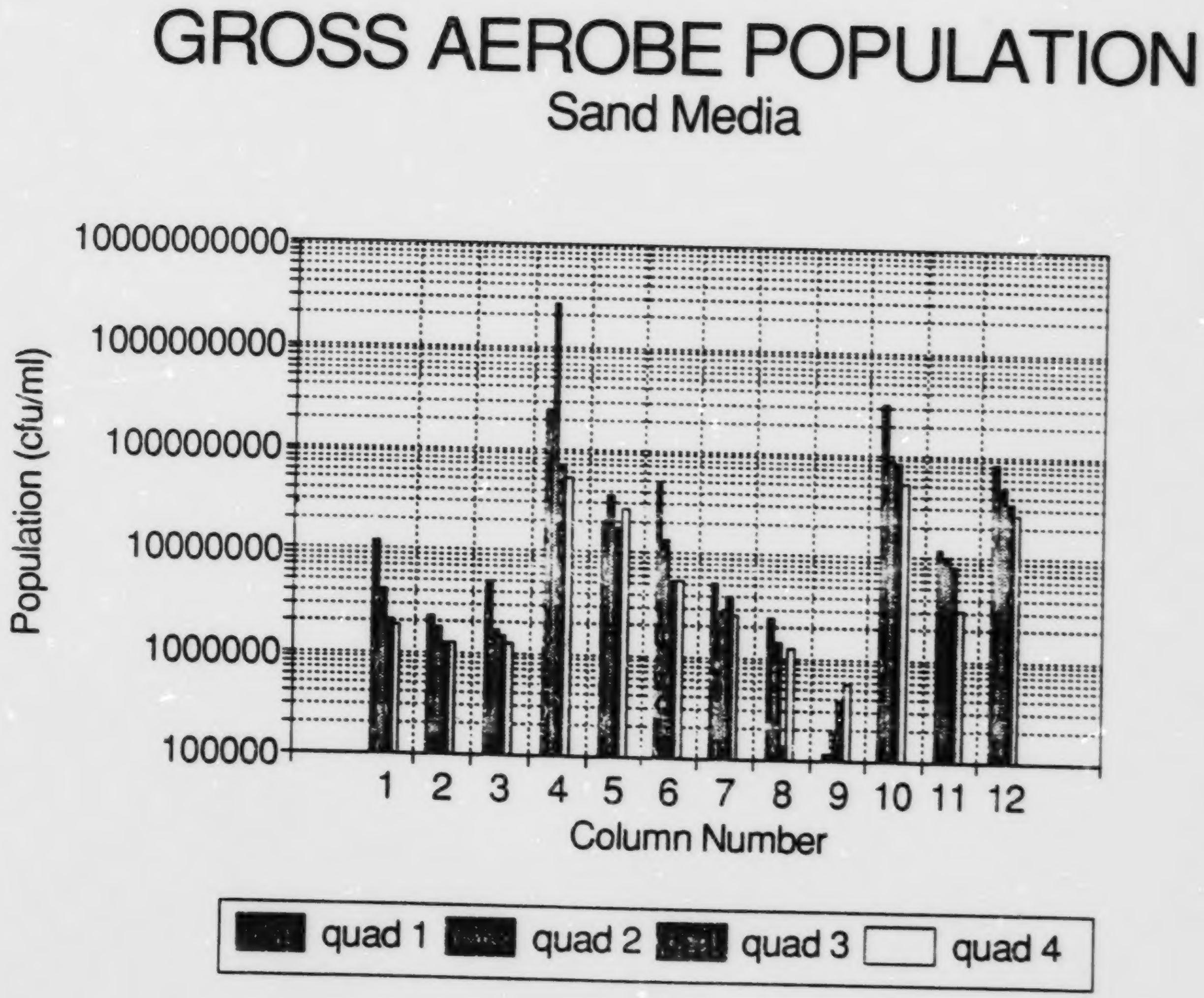

FIGURE 8 - GROSS AEROBE POPULATION

Gross aerobe populations are variable, although counts are generally higher in the nutrient enriched and plugged columns, especially for the two influent quadrants. This indicates a positive response to enrichment

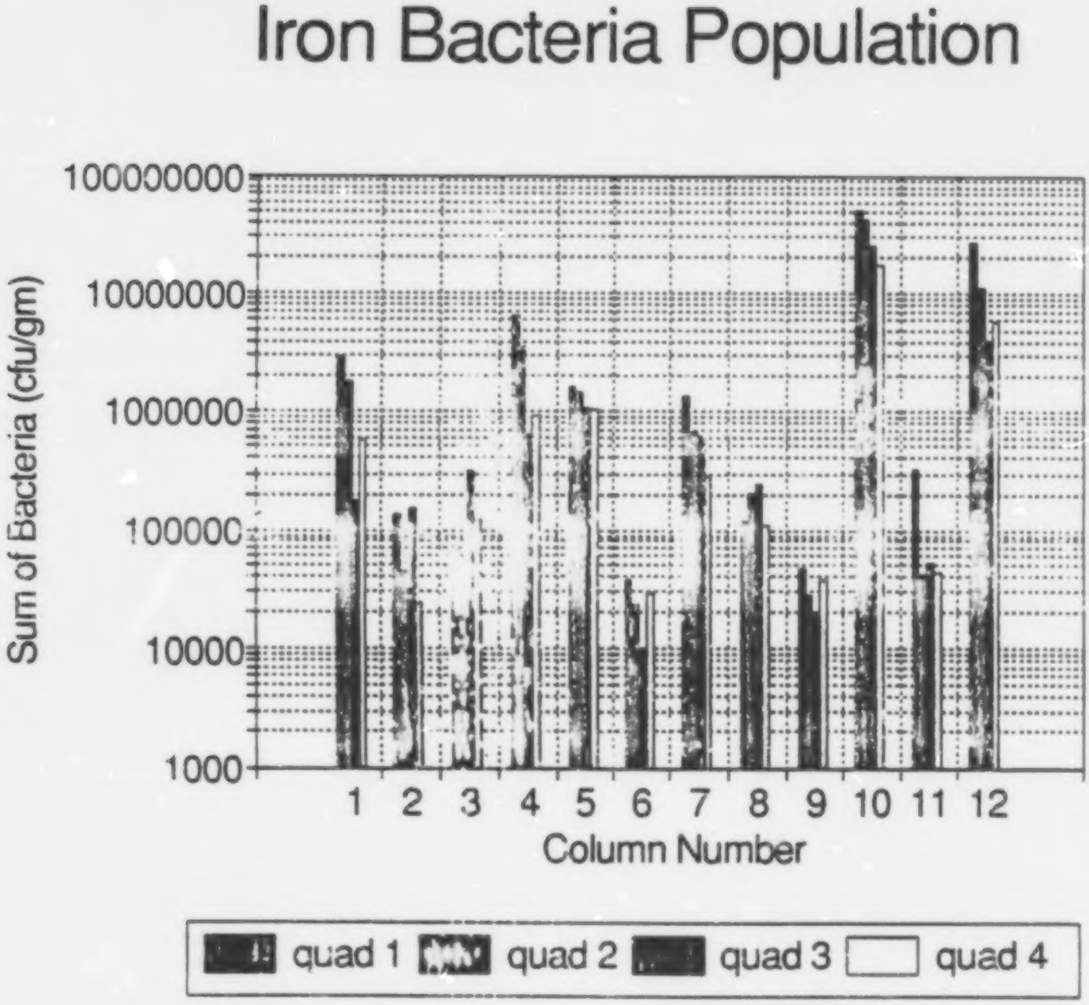

FIGURE 9 - IRON BACTERIA POPULATION

Iron bacterial populations vary with no consistent trend that relates to the addition of nutrients, including ferric citrate (FC, FAC)

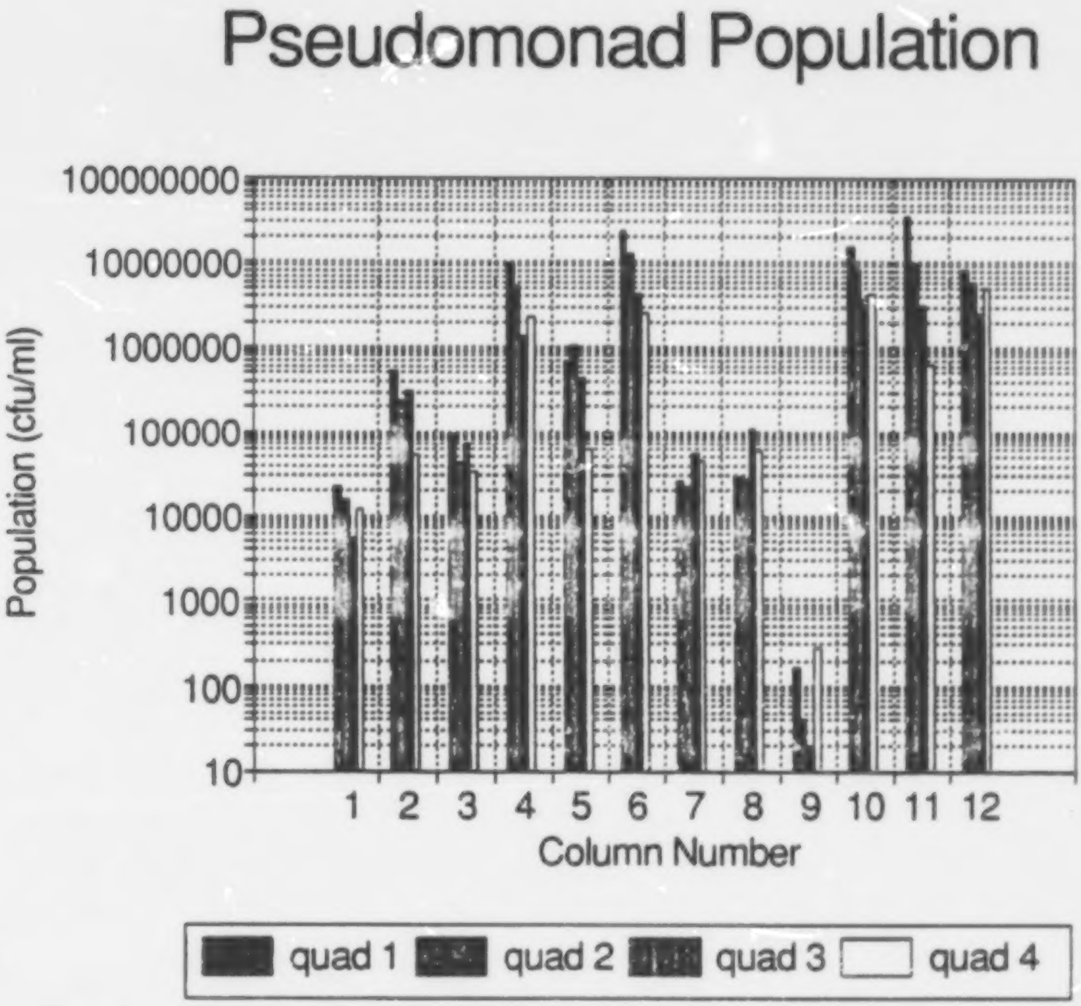

FIGURE 10 - PSEUDOMONAD POPULATION

Pseudomonad populations were consistently higher in the columns receiving nutrients and contaminants, i.e. 4, 5, 6, 10, 11, 12.

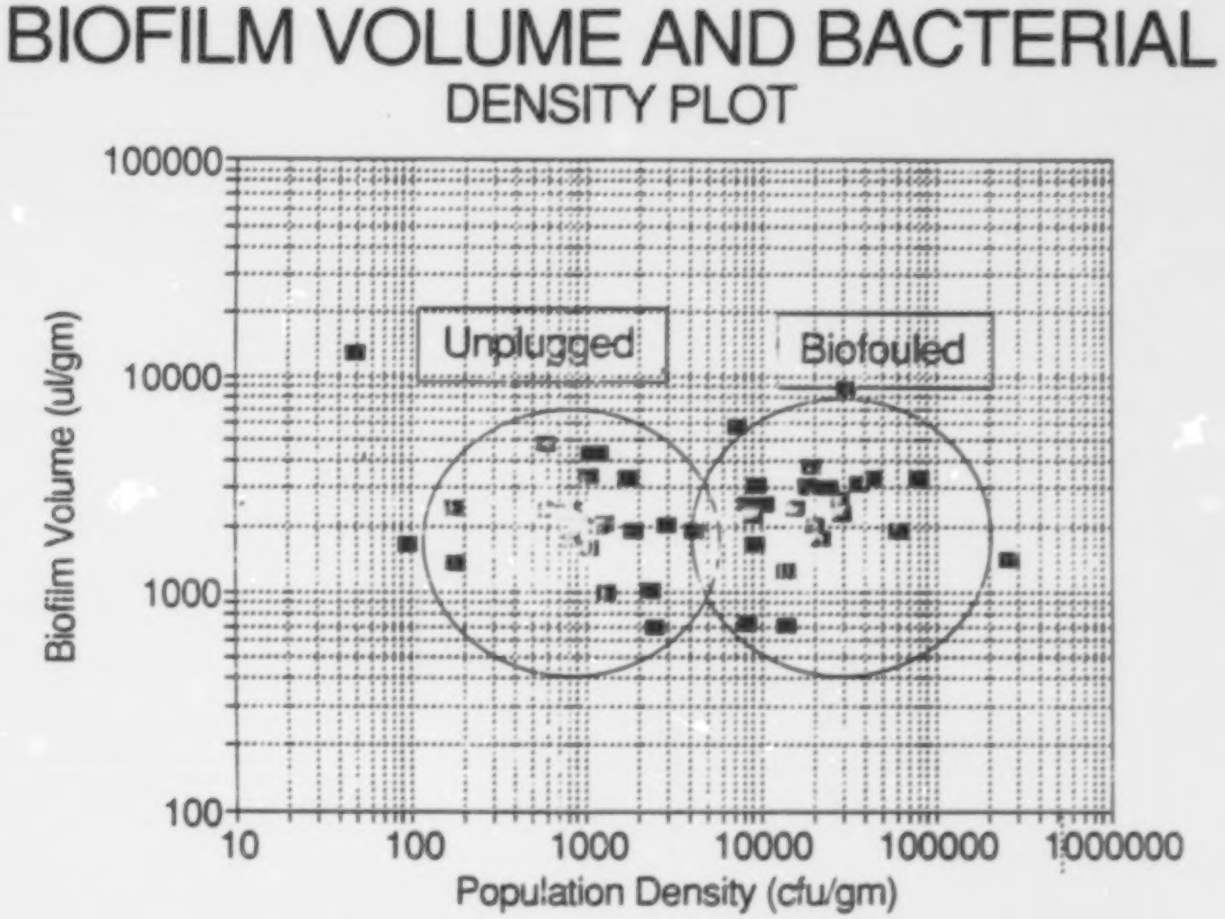

FIGURE 11 - BIOFILM VOLUME AND BACTERIAL DENSITY PLOT

Biofilm volume versus population density for each column quadrant yields two clusters. The plugged columns show consistently higher population densities.

of BTX, which will be addressed later; recalcitrance of the BTX relative to an unacclimated population, and natural avoidance of the BTX versus utilization of the citrate as an accessible carbon source. Toxicity does not appear to be a problem within the ranges of BTX used, and could be explained by the protective barrier provided by the exopolymeric matter of the biofilm (Costerton, 1983). Pseudomonads are adapted to the utilization of low molecular weight hydrocarbons (Eagon, 1980) which could well account for the elevated populations in the BTX plus nutrient enriched and plugged columns.

CONTAMINANT REMOVAL

Three contaminant substrates have been examined. Phenol was selected for preliminary tests due to its water solubility and relatively low volatility. As well, phenol concentrations can be rapidly and inexpensively analyzed. Phenol also has biocidal properties, yet is biodegradable following acclimation. BTX were selected as environmental contaminants of concern in petroleum products. A commercial gasoline was also used to test the ability of established biofilms to remove the hydrocarbons present.

Phenol

Phenol removal was assessed in preliminary tests using a gravel medium. Time series plots of phenol concentrations for an initially sterile control, simulated groundwater, and nutrient enriched groundwater are illustrated in Figure 12 The phenol losses in the sterile control were the least and the losses observed may be attributed to volatilization and possible biological uptake, since no attempt was made to preserve sterility. The data for the nutrient enriched case yield two curves. During the initial phases of biofilm growth, influent and effluent concentrations of phenol were the same. As the population adapted to the phenol and the biofilms expanded, phenol removal was rapid. The divergence of the influent and effluent phenol concentrations indicates that the biofouled media were effective in removing the contaminant.

The limited removal of phenol at the start could be attributed to several phenomena that require further analysis. The initial 140 mg/L concentrations used would have traumatized an unacclimated population, due to toxicity, recalcitrance of the molecule, and/or to excess carbon, since the contaminants were, in all cases, added before nutrients.

BTX

The column configuration used in the 40 column tests was the same as for phenol, with one exception. Sand was used in the BTX experiments, in part to facilitate rapid plugging of the media. This may have been a liability, along with the use of compounds that are volatile and have low water solubilities. For BTX, the results were dismal and inconclusive, due to solubility problems and massive abiotic losses. The design of the experiments was incompatible with

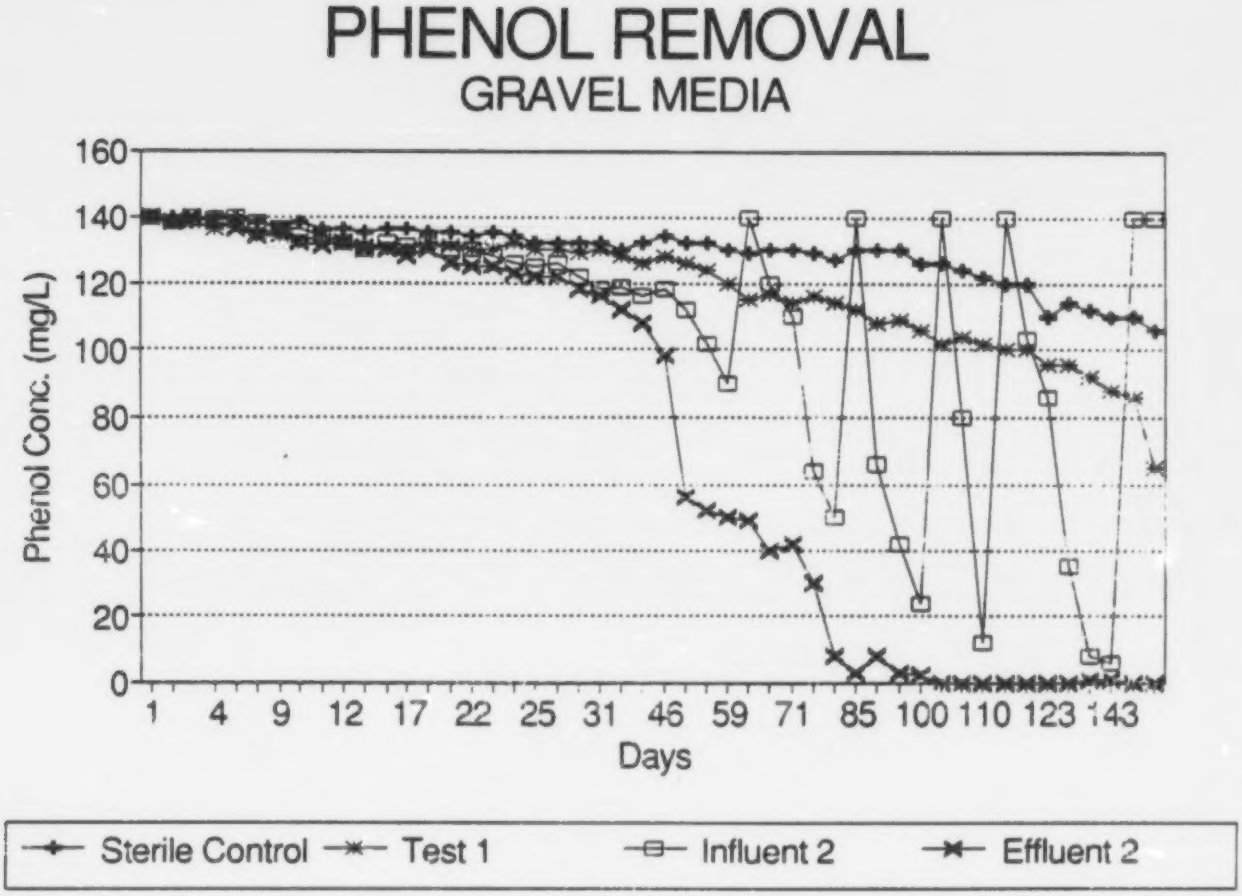

FIGURE 12 - PHENOL REMOVAL IN GRAVEL MEDIA

The data presented were derived from one experiment set, including a sterile control, groundwater, and a nutrient enriched system. The variability in the influent concentrations is due to repeated phenol additions of 140 mg/L. Effluent concentrations show rapid decreases as the biofilms mature in the third phase of growth. The sterile and Test 1 samples were obtained from effluent lines.

the goal of assessing BTX removal, due to the head spaces in feed tanks and head columns that allowed for volatilization of the contaminants. Secondly, the experiments were run without continuous agitation of the groundwater, thus facilitating the separation of the hydrocarbon-water phases. No demonstrable difference can be shown to prove that the biofouled media removed BTX. This can be illustrated by the plots for BTX (Figure 13) for a sterile control and a nutrient enriched column. Greater than 90% of the benzene was lost by abiotic mechanisms and accounts for the similar trends for the two cases. The difference in residual concentrations at 1.0 mg/L is too small to be significant. This pattern was typical for all runs using BTX.

As indicated above, use of a sand media to facilitate rapid plugging could be a major problem. For instance, in one experiment using 280 mg/L total BTX as the initial concentration, plugging was obtained in 3 days. As such, acclimation or adaptation to the BTX prior to rapid biofouling could well prevent removal of the contaminants.

Gasoline

One final set of experiments was set up to test whether or not a mature biofilm would remove a contaminant. In this case, gasoline was selected as the substrate. The microcosms used had been maintained in a biofouled state since 1988. Three systems were used, one dominated by iron related bacteria, and two dominated by sulphate reducing bacteria. The microcosms had been set up to assess biofouling and remediation techniques for water wells, and consist of 5.0 cm dia slotted well screens and an outer pea-gravel matrix. The model wells were disconnected from the feed systems, spiked with 2,000 mg/L gasoline, sealed with zero head space and shaken for 2 hours to ensure dispersal of the gasoline within the biofouled media. After the 2 hours, the wells were unsealed and sampled for water. Total petroleum hydrocarbon residuals in the water were 56 mg/L (IRB), and 8 mg/L and 20 mg/L (SRB). As a control, a 0.1 mL volume of gasoline was added to a 40 mL volume of distilled and deionized water in a 40 mL glass sample vial. The vial was shaken manually for 2 minutes at 5 minute intervals for 2 hours (total). The resultant analysis by GC-FID showed a concentration of 0.0025 mg/mL, or 100% of the initial spike. For the mature biofouled media, removal of the gasoline presumably occurred by uptake/assimilation, and possible transformation of the constituents. A biologically mediated removal mechanism is the most probable one, due to the lack of head spaces.

SUMMARY AND CONCLUSIONS

A basic experimental research project was initiated to demonstrate that biofouling of porous media can be induced by manipulating the availability of biofouling as a potential strategy for the in-situ containment of organic carbon,

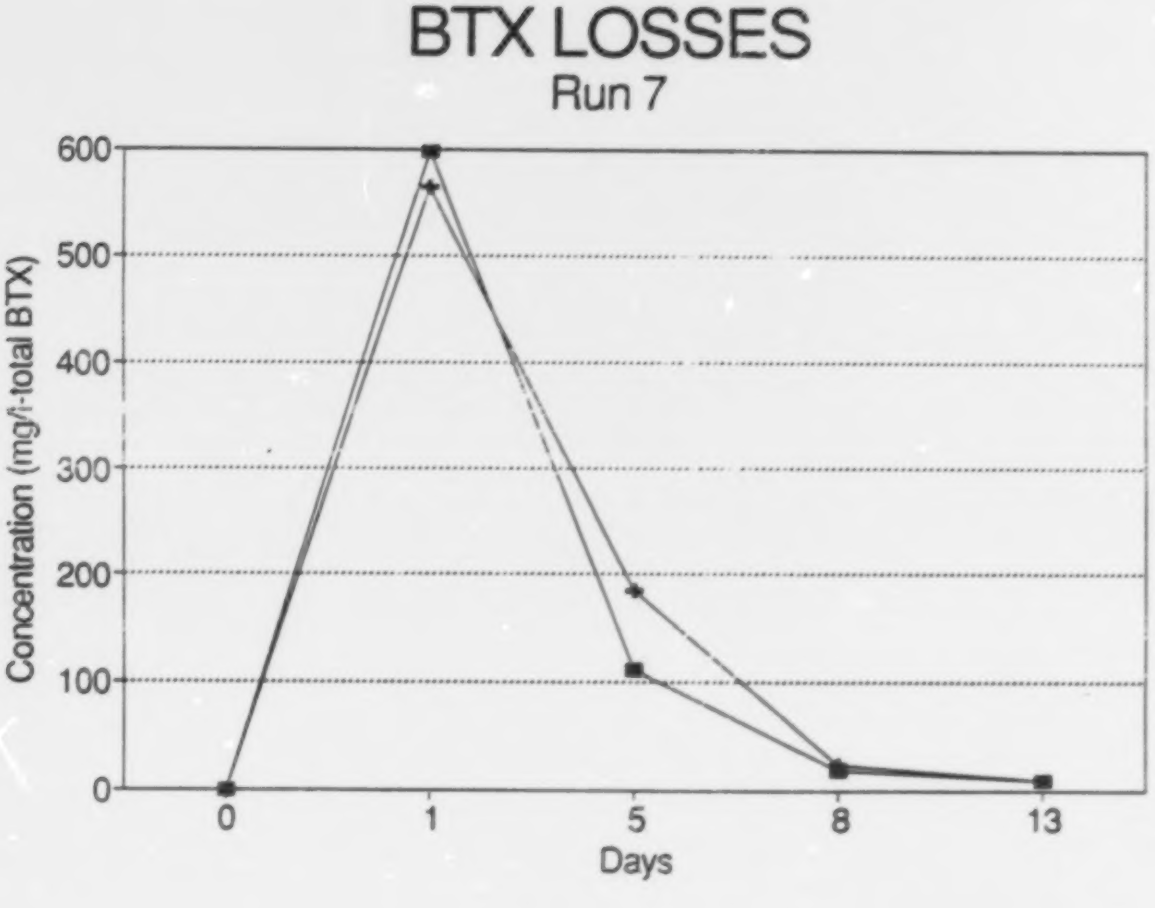

FIGURE 13a - BTX LOSSES

The plotted pcints for the nutrient enriched and sterile control show significant losses in both the columns that have been attributed to abiotic mechanisms, including liquid phase separation and volatilization. Plots for the individual BTX components are shown in Figures 13b, 13c, and 13d.

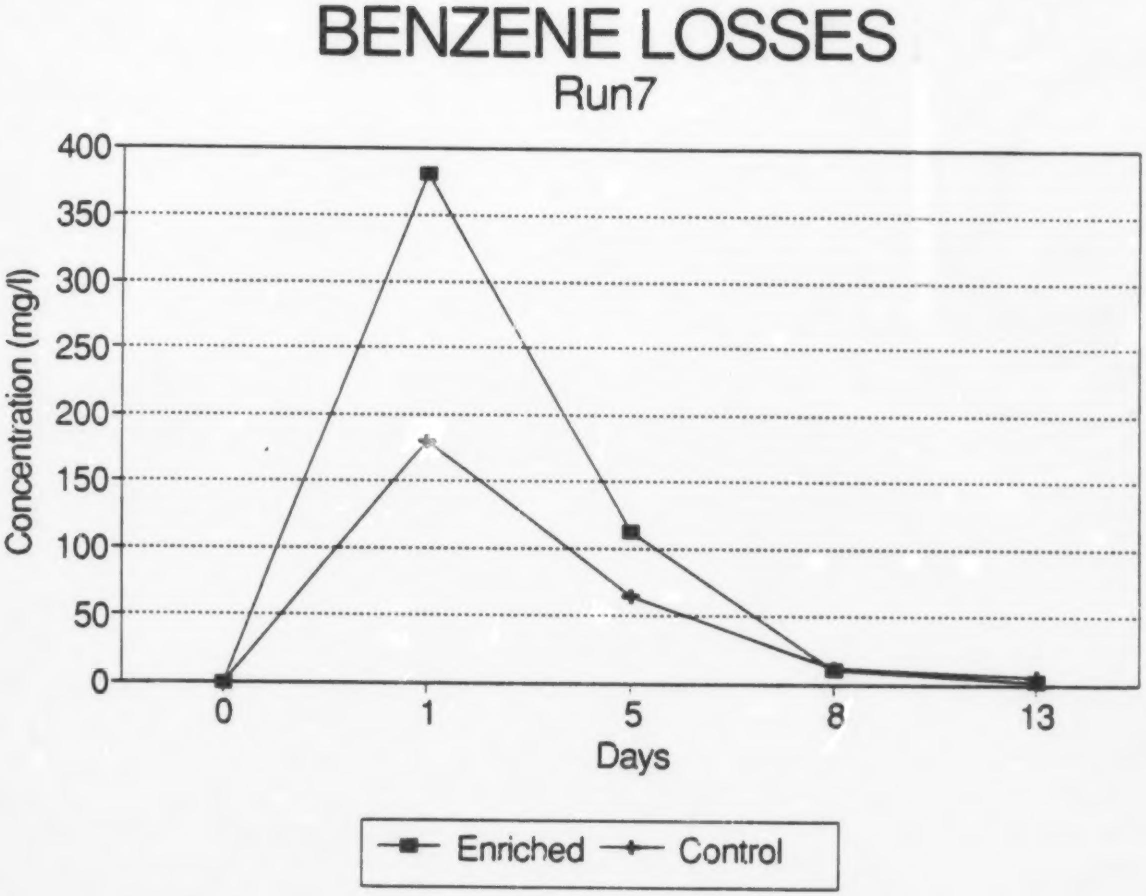

FIGURE 13b - BENZENE LOSSES

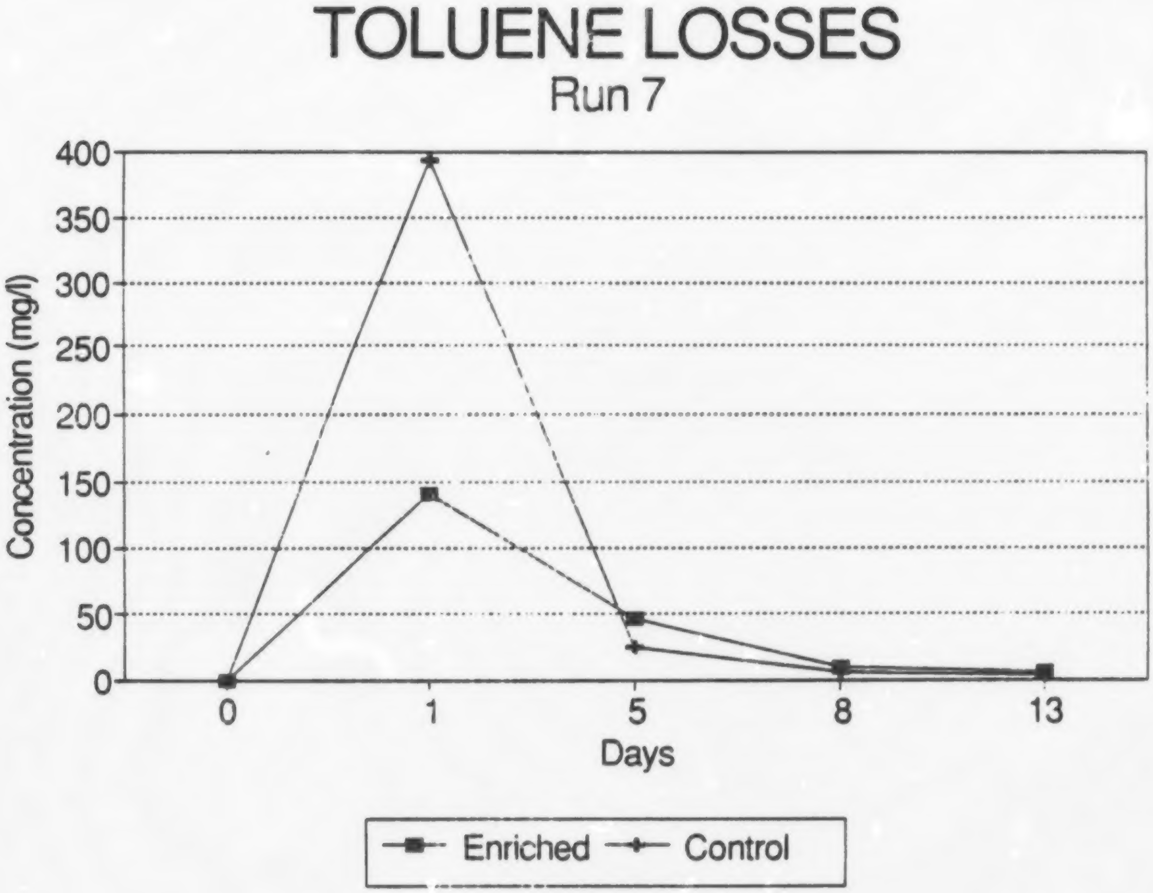

FIGURE 13c - TOLUENE LOSSES

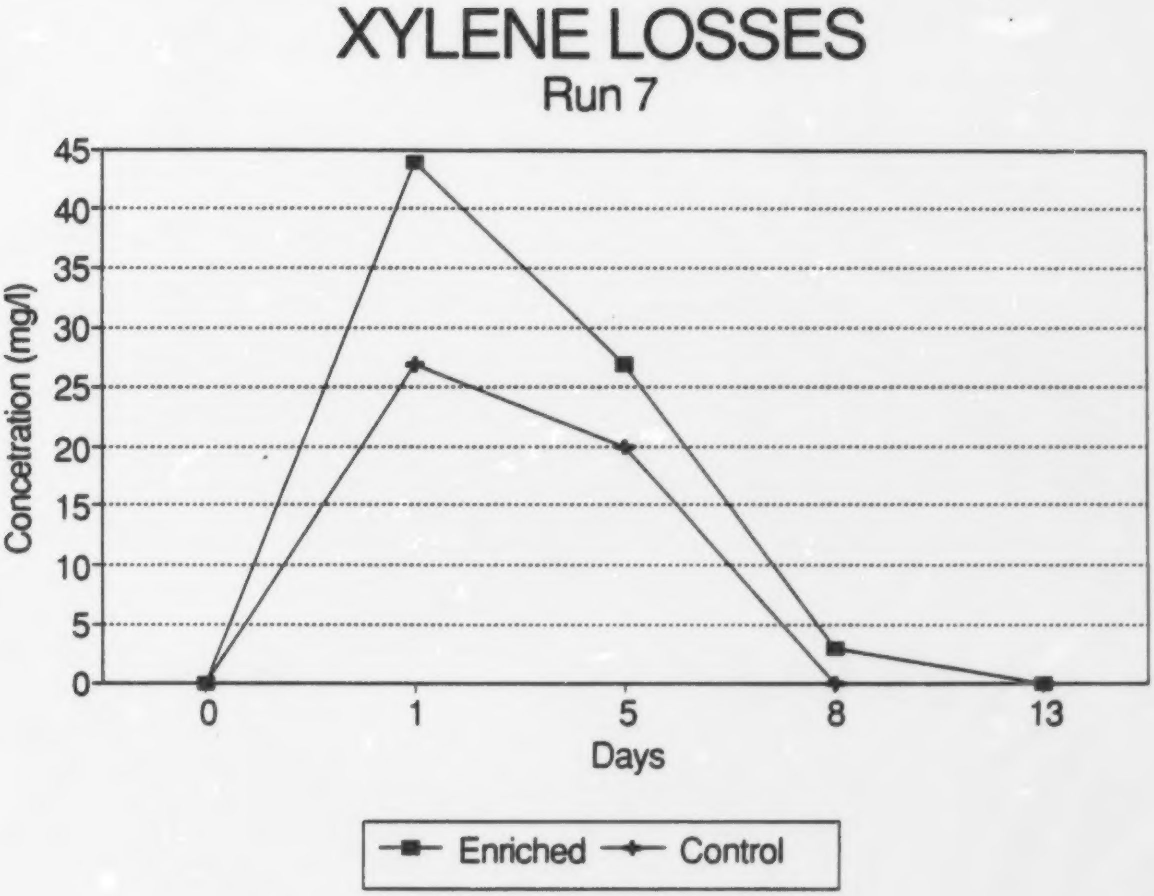

FIGURE 13d - XYLENE LOSSES

nitrogen and phosphorus. The purpose was to exploit contaminants in groundwater, and, secondly, to transform a portion of the aquifer into a fixed film bioreactor for the removal of the target contaminants.

In gravel media, at least four phases of biofilm growth leading to biofouling have been identified. These include initial log-phase growth associated with rapid colony and biofilm expansion; a second phase of biofilm contraction and possibly shearing; a third linear phase of slow growth with periodic pulsations, as indicated by flow data; and a fourth plateau phase characterized by a semi-stable minimum flow, and an evident shift from anaerobic to anoxic states. Experiments run with sand as a media show subtle initial reductions and possible pulsations in flow, with subsequent abrupt decreases in flow due to plugging. Replications, using moderate initial concentrations of phenol and BTX, have not shown significant inhibitory effects on the biofouling process.

Microbiologically, the experimentally fouled columns show higher population densities and bacterial loadings which would indicate a positive growth response to the carbon, nitrogen, and phosphorus applications. Biofilm volumes, while higher in the nutrient enriched columns, will be finite, due to the available pore volumes of the media. By combining data on the biofilm volume and population density, there are indications of fundamental structural differences that will account for the plugging of the media. In this case, the biofouled columns show higher bacterial loadings and population densities relative to the biofilm volume. In contrast, with similar biofilm volumes, the lack of plugging in the unenriched columns may be a function of higher proportions of weak exopolymeric matter that offers little resistance to flow. This is quite clear from the flow data for the unplugged columns that remained essentially constant throughout each experiment.

For phenol experiments, biological removal mechanisms have been indicated, based on the departure of concentrations between initially sterile controls and columns subject to nutrient enrichment. It is evident for these tests, at least, that, as the biofilm matures, and as the bacteria become adapted to phenol, removal is very rapid, with no detectable phenol passing through the barrier (within the analytical limits of the colorimetric test method). Data on BTX removal with sand media are inconclusive, except to show that abiotic losses are substantial. The problems have been attributed to the high volatility and low water solubility of these compounds. The system design used is clearly inadequate to demonstrate biological removal of BTX. A static test with zero head space and established biofilms was undertaken to assess the potential for petroleum hydrocarbon (gasoline) removal in view of problems encountered with BTX. In this case, more than 95% of the hydrocarbons was removed from the aqueous phase after 2 hours of continuous agitation. By comparison, a control experiment obtained a 100% recovery of the initial gasoline spike. Based on these latter, albeit limited results, biologically mediated removal of petroleum hydrocarbons is indicated.

Preliminary laboratory experiments have shown that porous media can be readily biofouled by providing a supply of organic carbon, nitrogen and phosphorus. Additional research is required to assess nutrient enrichment thresholds that lead to biofouling; microscopic analysis of biofilms in various stages of maturation and growth to account for variations in the removal of phenol, BTX and other target compounds: and refinements and/or alteration of the experimental design to improve the results on contaminant removal, including BTX.

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NITRATE ADDITION AS AN ALTERNATE ELECTRON ACCEPTOR FOR THE REMEDIATION OF ANAEROBIC BTEX CONTAMINATED GROUNDWATERS

by

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EXTENDED ABSTRACT

Gasoline contamination of the subsurface often produces a large volume of groundwater contaminated with the water-soluble components of gasoline, mainly the monoaromatic hydrocarbons, benzene, toluene, ethylbenzene and xylenes, termed BTEX as a group. Natural biodegradation results in minor removal of these organics but also in the removal of essentially all the oxygen that may have been present in the groundwater. Under anaerobic conditions BTEX biodegradation is thought to be slow or negligible. Thus, the contaminants continue to migrate in the anaerobic groundwater.

Remedial methods for such groundwater contamination include an in situ biological approach where oxygen is added to the groundwater to stimulate the aerobic biodegradation of the BTEX compounds. It is not known if some stimulation of the in situ microbial population could bring about their biodegradation under anaerobic conditions that are found in most actual incidents.

This research was undertaken to evaluate the possibility that BTEX could be degraded anaerobically by bacteria, specifically the bacteria involved in denitrification. If successful, this could produce a remedial strategy of stimulating the denitrifying bacteria in situ to degrade BTEX by the addition of nitrate. The critical compound in this evaluation is benzene. Its mobility in groundwater and very low regulatory action level, typically 5 ug/L, make it the contaminant of most concern in many situations of gasoline contamination of groundwater. The details of this research are provided in the M Sc project report of J. R. Barbaro (Univ. of Waterloo, 1990) and in a report to CPPI which is currently under review. In addition, two papers are being prepared for submission to a scientific journal.

Three natural-gradient injection experiments in the Borden aquifer, each 100 to 300 days duration, were used to evaluate the biotransformation of BTEX derived from gasoline under anaerobic, denitrifying conditions. The segment of the Borden aquifer used in this study was anaerobic, the result of a low-organic-loading leachate plume emanating from an abandoned landfill. The aquifer is composed of a rather uniform medium sand and the groundwater flows essentially horizontally at about 9 cm per day. The extensive hydrogeological and geochemical information base and the relative simplicity of the flow system make the Borden aquifer ideal for such natural-gradient injection experiments. The instrumentation at the field site is illustrated in Figure 1. Two such sites were established side-by-side. At one, the fate of BTEX from gasoline was followed without any remedial addition to act as an unremediated control experiment. At the other, nitrate was added to the BTEX-contaminated groundwater to evaluate the effect of this remedial addition. About every 10 days during each experiment, about 660 L of anaerobic groundwater was spiked with groundwater equilibrated with gasoline, with a conservative tracer (sodium bromide) and with nitrate where appropriate and then injected into the anaerobic segment of the aquifer. This created an essentially continuous source of dissolved contaminants, which migrated laterally at about 9 cm per day under the natural hydraulic gradient and in the natural, anaerobic biogeochemical environment. The approximate concentrations in the injected water were: bromide, 230 mg/L; nitrate 280 mg/L; benzene, 4500 ug/L; toluene, 2400 ug/L; ethylbenzene, 300 ug/L; m-xylene, 700 ug/L; p-xylene, 300 ug/L; o-xylene, 500 ug/L. The migration and fate of the injected chemicals were monitored via selected points in multilevel wells 1m upgradient of the injection well and 1m, 5m, and 20m downgradient.

A 452 day laboratory microcosm experiment was also conducted to aid in the interpretation of the field experiments. Anaerobic Borden aquifer sand and groundwater spiked with solutes were incubated in 60 mL hypovials stored in anaerobic chambers. Periodically, sets of hypovials were sacrificed for analysis. The disappearance of BTEX and nitrate in active microcosms that exceeded the disappearance in sterilized microcosms was interpreted as the result of biodegradation.

In the unremediated control field experiment toluene was biotransformed between the 1m and the 5m fences. Up to about 90% of the injected toluene was being removed after 200 days. All other compounds were recalcitrant. In the corresponding laboratory microcosm experiments all compounds, including toluene, were recalcitrant under unremediated anaerobic conditions.

After an acclimation period, toluene biotransformed relatively rapidly in the presence of nitrate in both the laboratory and field to an apparent threshold concentration of about 100 ug/L. This represents > 95% removal of toluene. In the presence of nitrate the xylene isomers and ethylbenzene biotransformed somewhat, generally with concentrations declining by less than 50% of the injected concentrations. Benzene was completely recalcitrant in all field and lab experiments. Essentially all of the biotransformation occurred within 1m of the injection well, much earlier than in the unremediated control experiment.

A few samples were checked for possible breakdown products or intermediates. Organic acids, including benzoic acids, at concentrations up to about 500 ug/L as well as several unidentified organics were detected at the 1m fence. None were present in the injected water and so they are considered to be produced in the biotransformation of the gasoline-derived organics. While these compounds do not appear to be as toxic as BTEX, their production and fate should be examined in subsequent experiments.

In both the field and laboratory experiments the active denitrification was confirmed via the acetylene block test, wherein the addition of acetylene blocks the conversion of nitrate to nitrogen gas with the accumulation of nitrous oxide which is measured. Interestingly, the addition of acetylene also blocked the biotransformation of toluene. This could indicate that toluene degradation is associated with the later conversions in the denitrification sequence; these later sequences are the ones blocked by acetylene addition.

An examination of the breakthrough curves in the nitrate-amended field experiment indicated that little organic contaminant mass loss was occurring beyond the 1m fence. However, nitrate concentrations continued to decline downflow to generally below 10 mg/L at the 20m fence. Clearly, denitrification is consuming other forms of organic substrates. This is encouraging because nitrate is a recognized contaminant and its remedial addition would raise concerns about nitrate levels after remediation ceases. These experiments suggest that denitrification can continue in anaerobic groundwaters provided other suitable organic substrates are available as they apparently were in the Borden aquifer.

In the later stages of the final injection experiment, the toluene concentration was raised stepwise in order to stimulated benzene biotransformation. It was observed that toluene was being quickly reduced in concentration and, if benzene could be cometabolized by bacteria growing on toluene, the lack of toluene beyond the 1m fence could have been limiting benzene biotransformation. Increasing toluene concentrations in the injection water from about 2400 ug/L, through 6800 ug/L to 14000 ug/L did not produce any benzene removal and in fact greatly inhibited the biotransformation of ethlybenzene and xylenes. Toluene degradation increased, but higher toluene concentrations, up to about 800 ug/L, were found. This confirmed the preference for toluene over the other aromatics by the in situ bacteria and confirmed the recalcitrance of benzene and the lack of its cometabolism during toluene utilization.

In addition to observations about BTEX fate under denitrifying conditions, these experiments provided exciting information on the inhibition of BTEX biotransformation in the presence of acetylene, the interactions between TEX biotransformations, the acclimation periods preceding in situ biotransformation, the fate of added nitrate, and BTEX migration rates. Through a comparison of the control and the nitrate-remediated field experiments it is concluded that the addition of nitrate brought about more and earlier toluene biotransformation, produced some ethylbenzene and xylene biotransformation, and did not result in a persistent plume of nitrate contamination. However, given the recalcitrance of benzene and the incomplete mineralization and high thresholds of the compounds that were biotransformed, the addition of nitrate as an alternate electron acceptor would not be sufficient as a remedial measure in this aquifer.

These results are in general agreement with the recent research into BTEX biodegradation under denitrifying conditions. The most reliable laboratory experiments confirm benzene's recalcitrance under denitrifying conditions in other sediment/water systems. Recent research to be reported at the In Situ and On-Site Bioremediation Symposium held in San Diego in March, 1991 found a similar recalcitrance of benzene when denitrifying bacteria were stimulated by nitrate addition. These studies include controlled laboratory experiments and monitoring at field sites where this remediation was attempted at a pilot scale. Significant benzene biodegradation has only been found in cases where oxygen seepage into the system with the resulting aerobic biodegradation of benzene could not be excluded. These studies and our studies at Borden are not encouraging for in situ bioremediation of gasoline-contaminated groundwaters using anaerobic, denitrifying conditions. Because the microbiology of the degradation of simple aromatic hydrocarbons such as BTEX under denitrifying conditions is not well understood, it is not possible to predict if the desired biotransformation can be stimulated. Until consistent, positive results are demonstrated, especially for benzene, the in situ bioremediation of BTEX contaminated groundwaters by stimulating denitrifying bacteria cannot be recommended as a viable approach.

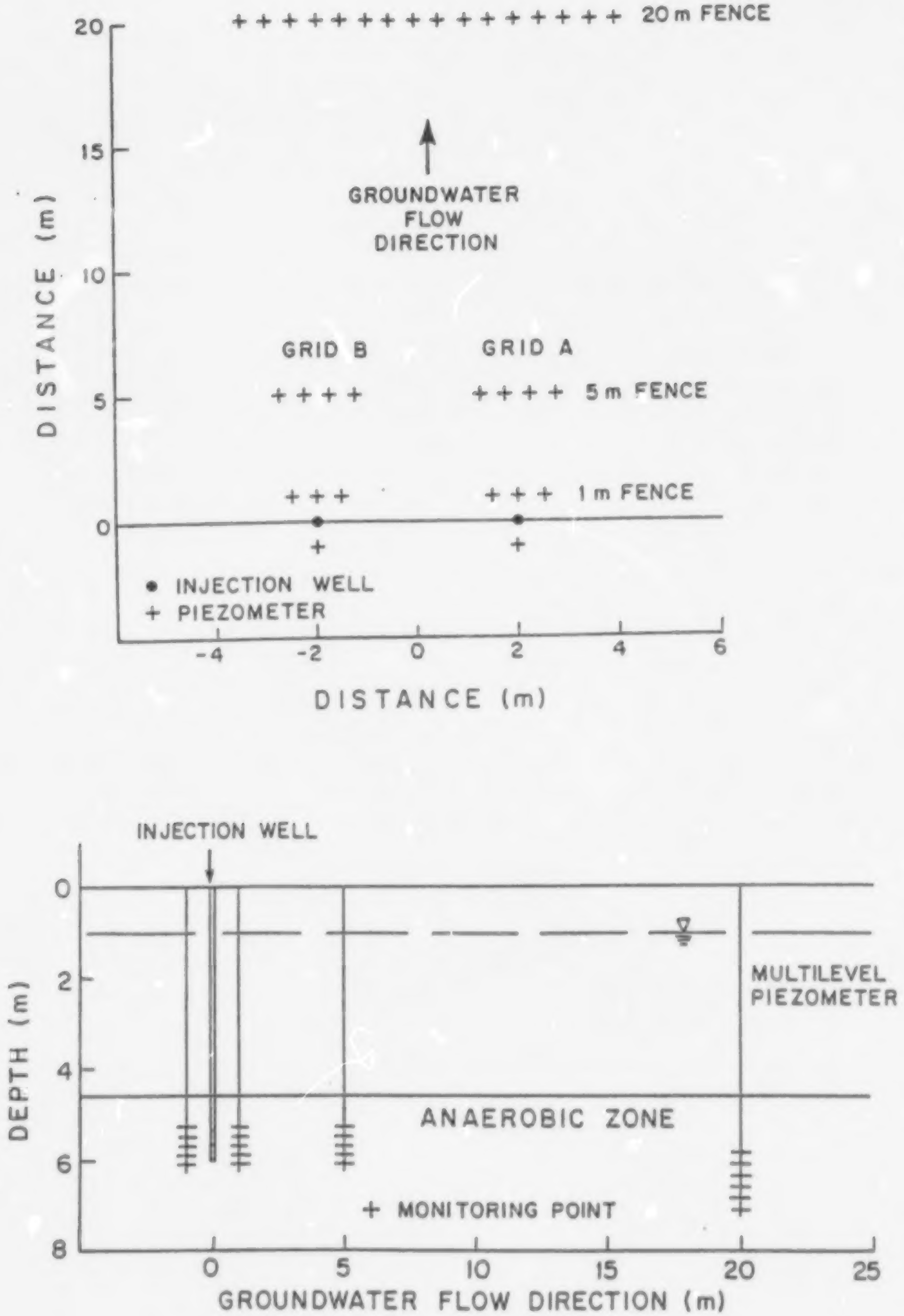
20m FENCE
GROUNDWATER
FLOW
DIRECTION
GRID B
GRID A
5 m FENCE
1 m FENCE
● INJECTION WELL
+ PIEZOMETER
DISTANCE (m)
20
15
10
5
0
-4
-2
0
2
4
6
DISTANCE (m)
INJECTION WELL
MULTILEVEL
PIEZOMETER
ANAEROBIC ZONE
+ MONITORING POINT
DEPTH (m)
0
2
4
6
8
0
5
10
15
20
25
GROUNDWATER FLOW DIRECTION (m)

Figure 1. Injection and monitoring grids: plan view (top) and cross-sectional view (bottom).

Current, Innovative and Emerging Excavate and Treatment Technologies for Contaminated Soils

By

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ABSTRACT

Approximately forty-five separate clean-up technologies were reviewed for their suitability to treat on-site excavated soil contaminated with petroleum hydrocarbons, wood preserving chemicals and chlorinated solvents. The technologies were described and categorized under the following main treatment technologies: thermal treatment, stabilization/solidification, soil washing, flotation techniques, solvent extraction, substitution and reduction-oxidation techniques, and biological treatment. General screening criteria were developed to establish priority ratings for research for the various technologies. A total of 8 individual technologies were given a medium-high or high research priority rating. Six of these technologies were discussed in more detail in terms of the technology process, the water treatment, the treatment rate, treatment costs and reported demonstrations.

1. INTRODUCTION

Approximately forty-five separate technologies were reviewed for their suitability for the on-site clean-up of excavated soil contaminated with petroleum hydrocarbons, wood preserving chemicals and chlorinated solvents. Information on various technologies was obtained from a search of appropriate data bases and letter and telephone interviews with key government agency personnel, researchers, and technology vendors in Canada, the United States, the Netherlands, West Germany, the United Kingdom, France, Denmark and Switzerland.

The quality of information varied from peer-reviewed publications of research findings and third party evaluation of technology demonstrations to non peer-reviewed conference proceedings and vendor technical bulletins.

Each technology was described in terms of the process and included a schematic of the process and approximate treatment costs; the types of waste and contaminant that the process could treat; a description of site applications and demonstrations of the technology; and a discussion for the need for further research, development and demonstration.

Finally all the technologies were summarized in tabular form and a general research priority rating was given to each technology.

A brief review of treatment technologies is provided in Section 2, of this paper, and a summary of technology, priority ratings for further research, development and demonstration is provided in Section 3. Section 4, discusses six selected emerging technologies which were given a high RD&D priority rating.

2. REVIEW OF TREATMENT TYPES

The clean-up technologies which were reviewed, were divided into four broad categories according to the dominant treatment process. These included; thermal treatment, physical treatment, chemical treatment and biological treatment. Table 1 summarizes the classification of treatment technologies for excavated contaminated soil.

Treatment technologies can also be categorized as destructive, separation, or immobilization technologies depending on the final disposition of the waste. Destructive technologies result in the chemical breakdown of the contaminant. Separation technologies do not destroy waste but separate the waste from the soil matrix resulting in a reduction of the volume of treatable waste. Immobilization technologies are non destructive and immobilize contaminants in an inert or stable material thereby reducing the impact of the contaminant on the environment.

Thermal treatment technologies include destructive incineration technologies and non-destructive separation and concentration technologies. Incineration technologies are capable of treating a wide range of organic compounds in solids, sludge and liquid waste feed. Rotary kiln incinerators, infrared incinerators and circulating bed combustors are commercially available as mobile units. These technologies are well understood and have been well demonstrated at field sites. Plasma arc/torch, heat soaking furnace, advanced electric reactor and molten salt are examples of incineration technologies currently under development. Non-destructive thermal technologies include the Taciuk process and low temperature thermal process technologies which use volatilization and distillation to separate contaminants from the soil matrix.

Stabilization/solidification technologies are non-destructive, immobilization technologies which involve the mixing of contaminated soil with reagents to form a low permeability and often solid material. Technologies include Portland cement and lime-based solidification, and clay stabilization.

Soil washing is an emerging technology in North America but is well developed in West Germany and the Netherlands where fixed and transportable systems have been operational for almost a decade. Soil washing is a non-destructive physical transfer process in which contaminants are separated from the soil by dissolution and dispersion processes using water alone, ultrasonic techniques or chemical additives such as surfactants.

Flotation techniques which utilize principles of particle surface chemistry and electric double layer theory are well known processes and have been used by the mining industry for the separation of ore metals from waste rock. The techniques have been recently applied to the clean-up of contaminated soils. The technique is non-destructive and separates the contaminant from the soil matrix. In some cases a recoverable and saleable product is produced which can offset the cost of treatment.

TABLE 1 TREATMENT TECHNOLOGIES FOR EXCAVATED CONTAMINATED SOIL

Thermal Treatment

- Thermal Destruction Technologies
  - Rotary-kiln
  - Fluidized Beds and Circulating Bed Combustors
  - Plasma Arc/Torch
  - Heat Soaking Furnace
  - Infrared
  - Oxygen Enriched
  - Advanced Electric Reactor
  - High Temperature Slagging Incinerator
  - Molten Salt
  - Industrial Processes
- Non-Destructive Thermal Technologies
  - Taciuk
  - Low Temperature Thermal Process

Chemical Treatment

- Solvent Extraction
  - Basic Extractive Sludge Treatment (B.E.S.T^{R}.) Process
  - Extraksol™ Process
  - Low Energy Extraction Process (LEEP)
  - BP Oil Solvent Extraction Process
  - Accurex Solvent Extraction Process
  - Soilex Process
  - EETD Solvent Extraction Project
  - CF Systems Process
- Substitution and Reduction-Oxidation Technologies
  - Dechlorination
  - APEG Process
  - Eco Logic Process
  - Chemical Oxidation

Physical Treatment

- Stabilization/Solidification
  - Portland Cement
  - Lime Based
  - Thermoplastics
  - Organic Polymer
  - Silicates
  - Clays
  - Glassification
  - Encapsulation
- Soil Washing
  - Classification and Washing
  - Soil Washing with Acids/Bases
  - Aqueous Surfactants
  - Chelating Agents
  - Steam Stripping
- Flotation
  - Agloflotation
  - Mosmans Method

Biological Treatment

- Landfarming
- Enhanced Landfarming
- Bioreactors

Solvent extraction technologies are non-destructive separation techniques which utilize organic solvents to solubilize organic contaminants from soil. Several of the technologies are commercially available and have been demonstrated at Superfund sites in the United States, while other technologies are still at the pilot-scale or laboratory-scale stage of development. Solvent extraction techniques are capable of treating a variety of waste types including soils and sludges.

Substitution and reduction-oxidation technologies are destructive technologies and are discussed under separate processes of dechlorination and oxidation. Dechlorination technologies include the addition of chemical reagents at ambient temperatures or the addition of hydrogen at elevated temperatures to dechlorinate toxic compounds. Dechlorination using alkali metal hydroxide and polyethylene glycol reagents (APEG) at ambient temperatures, has been used to treat PCB contaminated soil and chlorinated phenol contaminated sludge, and has been demonstrated at a number of sites in the United States. Dechlorination by hydrogen addition at elevated temperatures has been tested at the bench-scale. The process can treat PCB's and other chlorinated compounds in a variety of solid and liquid matrices. The technique was scheduled for demonstration to the Canadian Department of National Defense in 1990. Oxidation processes utilizing oxidants such as ozone and hydrogen peroxide are in various stages of development. Commercially available techniques which involve the mixing of hydrogen peroxide and synthetic polysilicate have been described for the clean-up of gasoline contaminated soil but a detailed field demonstration and critical review of the technology has not been documented.

Biological treatment technologies have been used for decades to treat oil refinery wastes, and are most effective in the treatment of light aliphatic and aromatic hydrocarbons. Heavier molecular weight PAH compounds and chlorinated organic compounds are more recalcitrant but can be treated under certain conditions. Under optimum conditions, biological treatment is a destructive technology. The simplest technologies are landfarming techniques in which the waste is spread over the ground and aerated using agricultural and construction equipment. Enhanced landfarming techniques involve piling the soil into mounds or windrows and enhancing biological activity through the use of soil amendments, forced aeration, heating and nutrient addition. Airborne emissions can be controlled by covering the soil. Bioreactors provide maximum control of environmental conditions since biological degradation occurs within an enclosed reactor vessel. The volume of soil that can be treated in each reactor batch is less than the volume that can be treated using enhanced landfarming techniques, but degradation rates are considerably faster.

3. ESTABLISHING RESEARCH PRIORITY NEEDS

3.1 Criteria for Rating Priorities

Technologies were rated for research and development support using a broad rating system of high, medium or low priority, according to the following general criteria:

High Priority
- technology is capable of treating high volumes of waste at low cost
- technology has been proven effective elsewhere but has not been demonstrated in North America

	• technology is still in the developmental stage and has potential for application
Low Priority	• technology is well understood and well developed • technology is commercially well developed and well demonstrated • technology is no longer being actively developed or pursued • technology has severe limitations (eg. process too expensive, low treatment rates, low treatment effectiveness, technology cannot be made mobile)
Medium Priority	• contains some combination of criteria found under both high and low priority ratings

3.2 Summary of Priority Rating

Destructive thermal technologies are generally well understood processes and many have been demonstrated under field conditions. Further research relates to refinement of the process to increase treatment capacity and improve waste feed handling. Consequently, these technologies are given a low priority rating.

Non-destructive thermal technologies are capable of treating large volumes of waste contaminated with volatile petroleum hydrocarbons. These technologies have been given a low to medium-high research priority rating.

Solidification/stabilization technologies are commercially well established and while they are effective in treating metals, their ability to immobilize organic compounds has not been proven. As well, long term evaluation of the effect of freeze/thaw cycles prevalent under Canadian climatic conditions is needed. Solidification/stabilization technologies often result in an increase in the volume of treated waste because of the addition of reagents. These technologies have generally been given a low priority rating with the exception of clay stabilization which shows some potential for stabilizing organic compounds and is given a medium priority rating.

Soil washing technologies are used extensively in Germany and the Netherlands but have only recently been demonstrated in North America. Soil washing works best with coarse grained soils, but research is required on improving the separation of heavy molecular weight organics in fine grained soils. The use of surfactants in the soil washing process to enhance solubilization of organic compounds is still in the developmental stage and this technology has been given a high research priority rating.

Flotation methods have the potential to treat large quantities of contaminated soil and are based on well established mine processing technology. The process is commercially developed in the Netherlands. The Agloflotation™ process developed by Alberta Research Council shows promise as an economical soil clean-up method. This technique utilizes coal in the treatment process and produces a combustible agglomerated residue which may have some economic value. Further research is required to evaluate the capabilities of the process to treat a range of contaminant feed types and to evaluate the extraction efficiency for a range of organic compounds at field scale.

Solvent extraction technologies are promising technologies for reducing the volume of contaminated soil. However, further evaluation of the range of contaminants and feed types that can be processed is required. Several technologies including the BEST., Extraksol, BP Oil and CF Systems are well developed commercially but require further field scale demonstrations and have been given a medium research priority rating. The

LEEP and Accurex processes have been given a high priority because they are currently at the bench-scale stage of development and more development and demonstration of the technologies are required before these processes can be properly evaluated.

Dechlorination techniques are specific to the treatment of chlorinated compounds. The APEG process requires further evaluation of the effect of adsorbing materials in soils such as clays and organic matter, on the process efficiency, as well as the identification and toxicity of transformation compounds. However, the technology is well supported commercially and has been demonstrated at several sites including a Superfund site. Consequently it has been given a low priority rating. The Eco Logic process is a thermal dechlorination technique which destroys chlorinated organics at efficiencies similar to incineration at costs significantly lower than incineration. This technology has been tested in a number of bench-scale tests but an evaluation of the technology under field conditions has not yet been reported. This technology has been given a high priority rating due to promising results of bench-scale testing and its ability to treat both aqueous and solid matrices.

Oxidation of contaminated soil using hydrogen peroxide and ozone are in various stages of development. One commercial process known as LANDTREAT has been used in California to treat soils contaminated from hydrocarbon spills. Evaluation of this technology under Canadian conditions is needed as well as an evaluation of contaminant losses from biodegradation, volatilization, leaching and photolytic degradation. This technology was given a medium priority rating.

Biologic treatment techniques particularly enhanced landfarming and bioreactors are well documented destructive technologies. Further research is required to; optimize conditions for the biodegradation of heavy molecular weight and chlorinated organic compounds, improve contaminant transfer through the use of solvents or surfactants, quantify contaminant losses through abiotic processes and identify transformation products. Landfarming is a well established technique but difficulty with the quantification of abiotic losses presents a problem with properly evaluating the effectiveness of the technique. Landfarming was given a low priority rating. Enhanced landfarming techniques allow greater control of environmental conditions and abiotic losses and were given a medium priority rating. The development of bioreactors is undergoing considerable research, particularly in the Netherlands, but mobile, commercial units are available. Bioreactors allow even greater control of process conditions than enhanced landfarming techniques and allow a critical evaluation of process effectiveness. Consequently, bioreactor technology was given a high research priority.

Table 2 summarizes the development stage and research priority rating for the various technologies.

4. EXAMPLES OF SELECTED EMERGING TECHNOLOGIES

A total of 8 individual technologies were given a medium-high or high research priority rating. Six of these technologies including: the non destructive thermal Taciuk process, soil washing with aqueous surfactants, Agloflotation^{TM}, solvent extraction using LEEP, dechlorination using the Eco Logic process, and bioreactors are briefly described below.

Table 2 RESEARCH PRIORITY RATINGS FOR SOIL CLEAN-UP TECHNOLOGIES

Process	Development Stage	Research Priority
THERMAL TREATMENT TECHNOLOGIES		
Rotary Kiln	Commercial	Low
Circulating Bed Combustors	Commercial	Low
Plasma Arc/Torch	Bench-scale	Low-Medium
Heat Soaking Furnace	Bench-scale	Low-Medium
Infrared	Commercial	Low
Oxygen Enriched	Commercial	Low
Advanced Electric Reactor	Pilot-scale	Low
High Temp. Slagging	Pilot-scale	Low
Molten Salts	Bench-scale	Low-Medium
Taciuk	Commercial	Medium-High
Low Temperature Thermal	Commercial	Low
PHYSICAL TREATMENT TECHNOLOGIES		
Portland Cement Solidification	Commercial	Low
Lime Based Solidification	Commercial	Low
Thermoplastics (Asphalt Batching)	Commercial	Low
Organic Polymer Solidification	Commercial	Low
Silicate Solidification	Commercial	Low
Clay Stabilization	Bench-scale	Medium

Table 2 RESEARCH PRIORITY RATINGS FOR SOIL CLEAN-UP TECHNOLOGIES

Process	Development Stage	Research Priority
Glassification	Commercial, pilot-scale	Low
Encapsulation	Commercial	Low
Soil Classification and Washing with Water	Commercial	Medium
Soil Washing with Acids and Bases	Commercial	Medium
Aqueous Surfactants	Commercial, pilot-scale	High
Chelating Agents	Commercial	Low
Steam Stripping	Pilot-scale	Medium
Agloflotation™	Commercial, pilot-scale	High
Mosmans Method™	Commercial	Low-medium
CHEMICAL TREATMENT TECHNOLOGIES		
B.E.S.T.™	Commercial	Medium
Extraksol™	Commercial	Medium
LEEP	Commercial	High
BP Oil	Commercial	Medium
Accurex	Bench-scale	High
Soilex	Pilot-scale	Low-medium

Table 2 RESEARCH PRIORITY RATINGS FOR SOIL CLEAN-UP TECHNOLOGIES

Process	Development Stage	Research Priority
EETD	Bench-scale	Medium-High
CF Systems	Commercial	Medium
APEG	Commercial	Low
Eco Logic	Commercial, pilot-scale	High
LANDTREAT	Commercial	Medium
BIOLOGICAL TREATMENT TECHNOLOGIES		
Landfarming	Commercial	Low
Enhanced Landfarming	Commercial	Medium
Bioreactors	Commercial	High

4.1 Taciuk Process

The Taciuk process is a non-destructive thermal process which was developed in 1975 by the Alberta Oil Sands Technology and Research Authority (AOSTRA) and the Industrial Processes Division of UMA Engineering Ltd., to extract and upgrade oil products from oil sands and oil shales.

The major component of the Taciuk system is a horizontal rotating chamber which treats contaminated soil in four stages: preheating, reaction, combustion and cooling.

In the pre-heat stage, volatile organic compounds and water are removed at temperatures of up to 260°C. Oils and heavy volatiles are distilled during the reactive stage at temperatures between about 370°C - 625°C in a pyrolytic environment. A coke byproduct which forms on the soil is burned off in the reaction stage, at temperatures between about 600°C - 815°C. (Turner 1989). The decontaminated soil is then cooled and conveyed to a tailings pile for later backfilling on-site. The distilled contaminant hydrocarbon is further treated to produce a product that may have some economic value as a re-usable product or may require alternate disposal. A schematic of the process is given in Figure 1.

The Taciuk process is capable of treating hydrocarbon contaminated soils and chlorinated hydrocarbon wastes. The technology is being commercially developed by Soiltech Inc. who have constructed transportable and fixed plants with feed rates ranging from 3-25 tonnes/hour (Soiltech Inc. undated). Estimated treatment costs range from $60 - $140/tonne (Turner 1989), and assume some saleable byproduct, but do not include feed preparation costs or final product disposal costs.

The technology has been demonstrated on heavy oil production wastes (Turner 1989), blended oil refinery wastes (Bowman 1988) and PCB contaminated soils (Soiltech undated). Concentrations of volatile organic compounds and heavier polynuclear aromatic hydrocarbons (PAH's) in treated soils were generally below limits of detection. The process recovered between 93 - 95% of PCB's in short duration tests.

The process needs to be evaluated under field conditions and is currently being demonstrated at a superfund site in Wisconsin (H. Melcer - Environment Canada, personal communication).

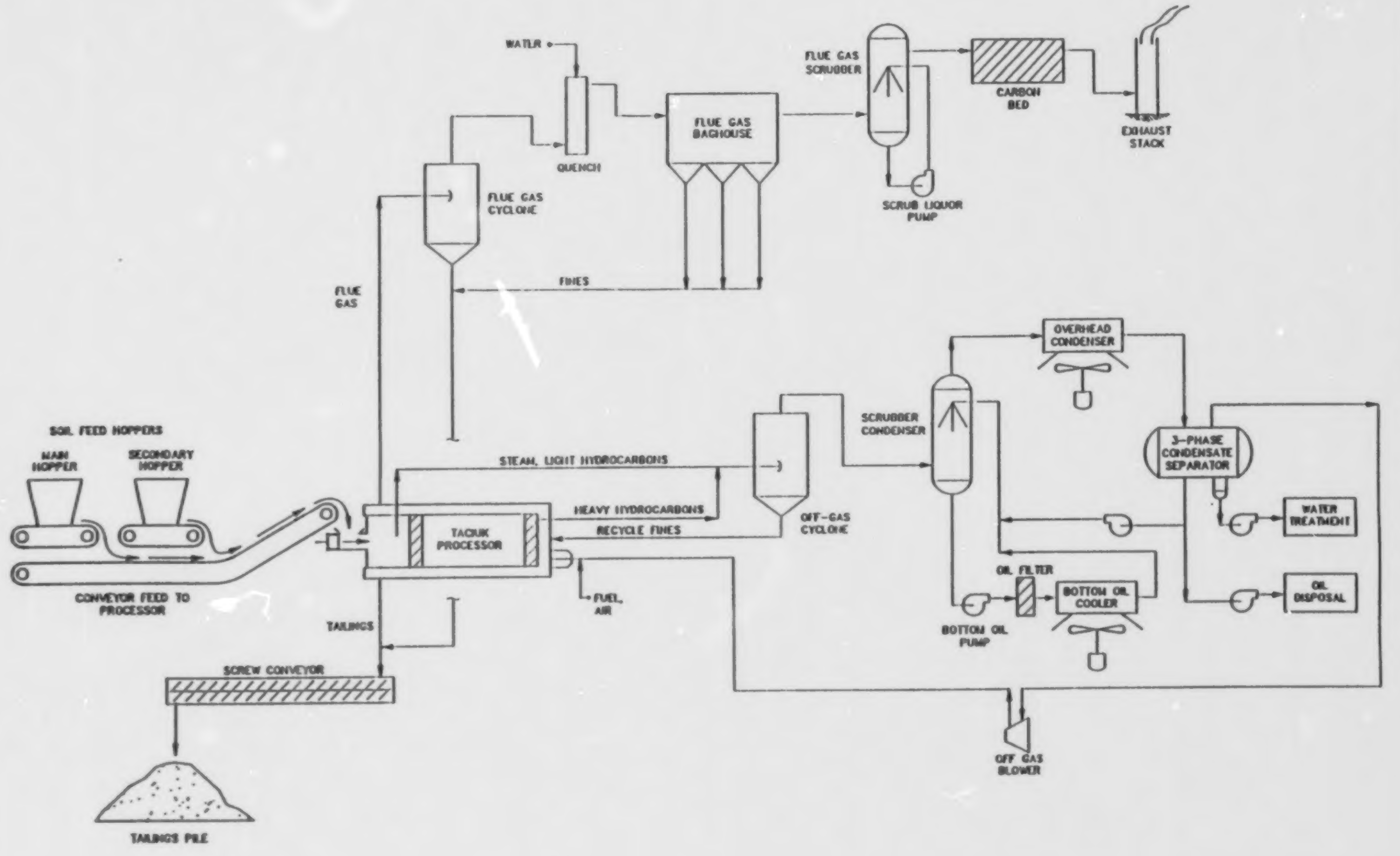
4.2 Soil Washing Using Aqueous Surfactants

Soil washing technologies are non-destructive separation technologies which are well developed in West Germany and the Netherlands and are now emerging in the United States and Canada.

The addition of aqueous surfactants or surface active agents to the washing process facilitates the separation of organic contaminants from soil particles.

In general the process consists of the pretreatment of contaminated soil to remove large objects and crush hardened soil. The soil is then thoroughly mixed and agitated in a reactor vessel which contains the washing fluid. This process transfers the contaminants from the soil particles to the washing fluid. The washed material is then separated into a coarse solids and liquid fraction, a fine solids and liquid fraction, and a foam fraction. The coarse solids are dewatered and disposed of as clean fill, while the fine sediment fraction containing concentrated contaminated waste and the foam is sent for final disposal.

A schematic of the process is given in Figure 2 and is described by Beers (1987).


WATER
QUENCH
FLUE GAS BAGHOUSE
FLUE GAS SCRUBBER
CARBON BED
EXHAUST STACK
SCRUB LIQUOR PUMP
FLUE GAS CYCLONE
FLUE GAS
FINES
OVERHEAD CONDENSER
SCRUBBER CONDENSER
3-PHASE CONDENSATE SEPARATOR
WATER TREATMENT
OIL DISPOSAL
OIL FILTER
BOTTOM OIL COOLER
BOTTOM OIL PUMP
OFF GAS BLOWER
SOIL FEED HOPPERS
MAIN HOPPER
SECONDARY HOPPER
STEAM, LIGHT HYDROCARBONS
HEAVY HYDROCARBONS
RECYCLE FINES
TACIUK PROCESSOR
OFF-GAS CYCLONE
CONVEYOR FEED TO PROCESSOR
FUEL, AIR
TAILINGS
SCREW CONVEYOR
TAILINGS PILE

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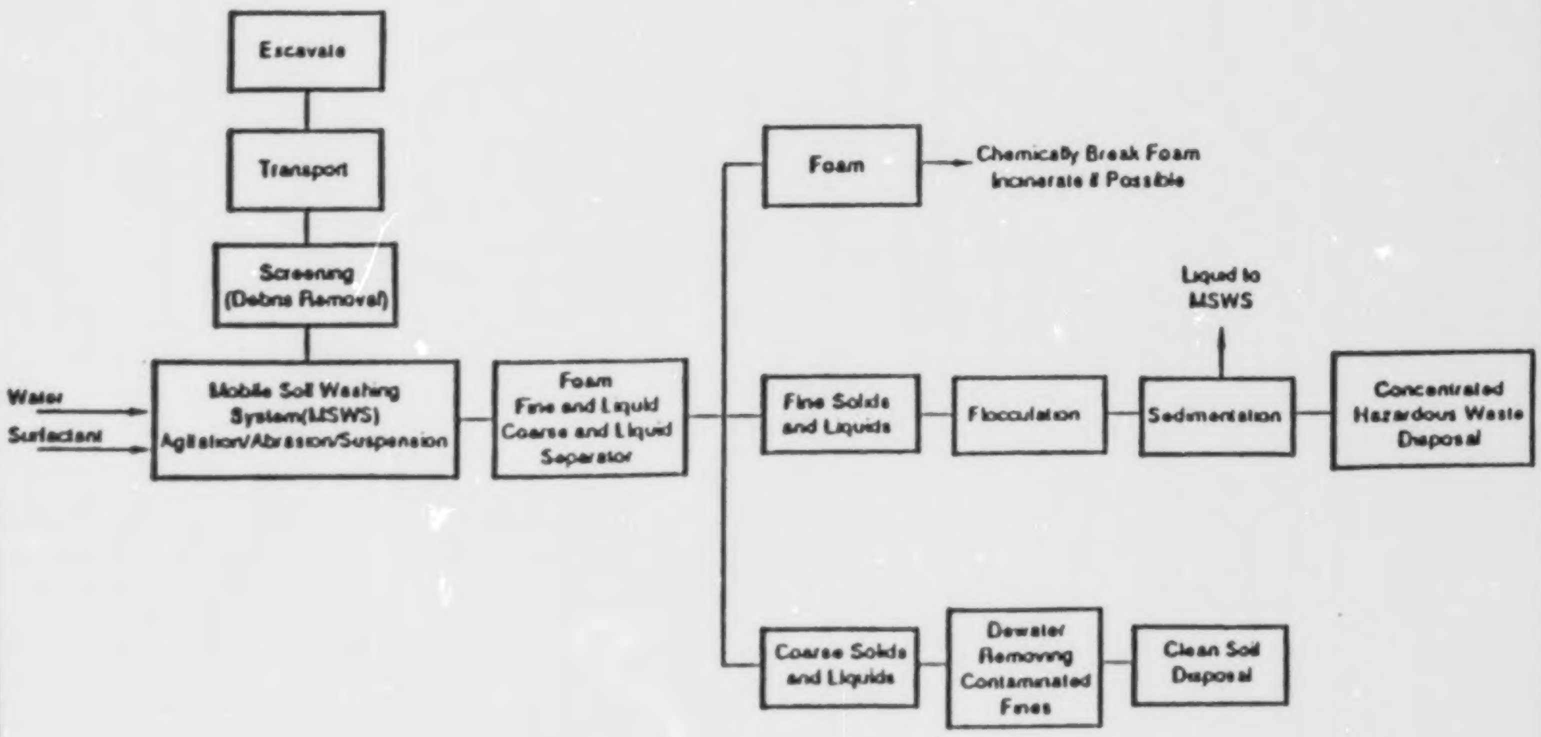
THE TACIUK PROCESSOR (Soil Tech, undated)

Figure 1.


Escavate
Transport
Screening (Debris Removal)
Water
Surfactant
Mobile Soil Washing System(MSWS) Agitation/Abrasion/Suspension
Foam Fine and Liquid Coarse and Liquid Separator
Foam
Chemically Break Foam Incinerate if Possible
Fine Solids and Liquids
Flocculation
Sedimentation
Liquid to MSWS
Concentrated Hazardous Waste Disposal
Coarse Solids and Liquids
Dewater Removing Contaminated Fines
Clean Soil Disposal

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USEPA MOBILE SOIL WASHING SYSTEM PROCESS SCHEME FOR SOIL WASHING WITH SURFACTANTS (After Beers, 1989)

Figure 2

The USEPA have developed a mobile soil washing unit which is capable of treating 4 - 8 tonnes/hour and has been tested at a pilot scale. Treatment costs are not available.

Soil washing using surfactants have been used to treat soils contaminated with oil, distillate hydrocarbons and PCB's (Ellis et al 1985), chlorinated hydrocarbons (Clement et al 1986), volatile and semi-volatile organic compounds (Esposito et al (1989), Trost 1987) and pentachlorophenol (PCP) (Coles et al 1989).

Percent removal of organic contaminants ranged from 85 - 100% for soil washing solutions containing 0.5% to 2% surfactant.

Soil washing technologies are most effective for coarse grained sandy soil. Soil containing high proportions of silts and clays may prove problematic though Esposito et al (1989) report treatment of soils containing 28% silt and 12% clay.

Full scale field demonstrations of the technology are required to evaluate its effectiveness.

4.3 Agloflotation™ Process

The Agloflotation™ process is a non-destructive separation technology which is being developed by Alberta Research Council and the Electric Power Research Institute. The process utilizes principles of froth flotation to separate contaminants from soil particles and the process is enhanced by the addition of fine grained coal particles.

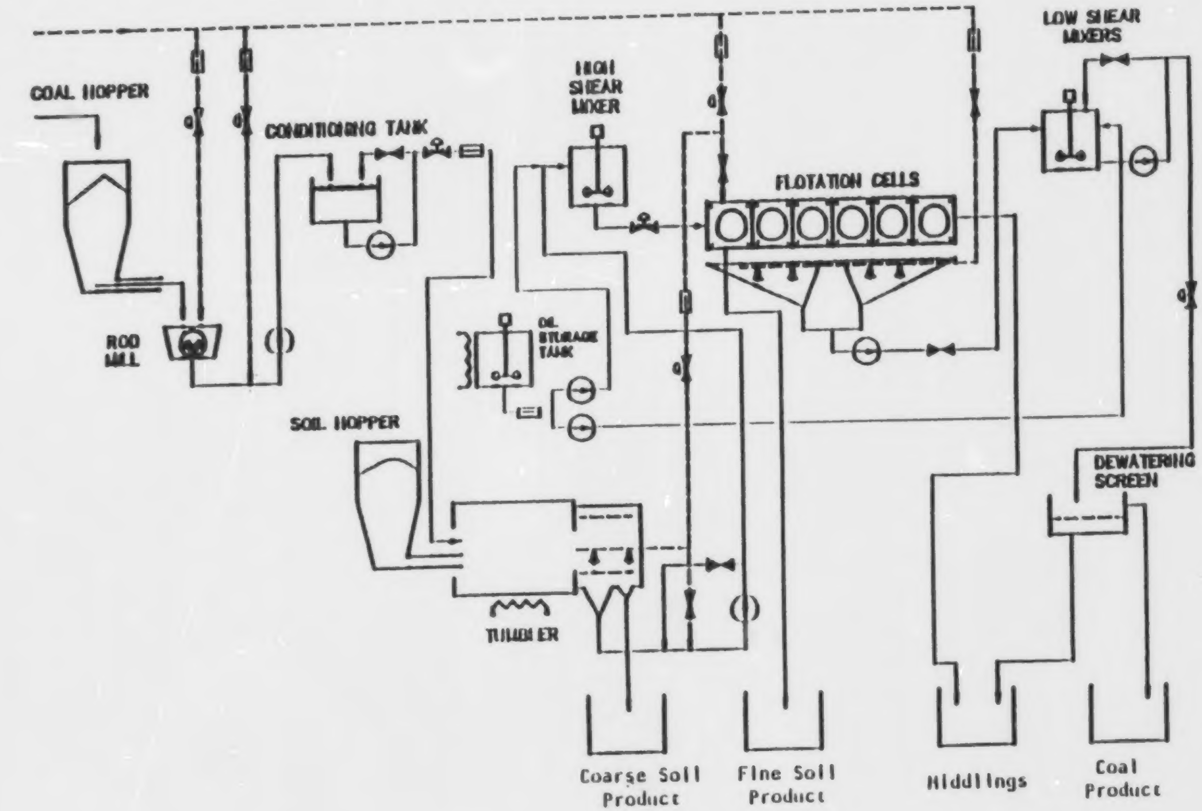
The technology consists of four main system processes including: coal particle and waste material preparation and contact; waste stream separation; coal/contaminant agglomeration and dewatering; and dewatering of cleaned solids.

Coal is milled to a fine particle size and mixed with water. The slurry is fed to a tumbler unit where it is mixed with contaminated soil feed. During this stage, contaminants are easily removed from coarse grained soil particles and adsorbed onto the coal fines. The coarse (> 1mm) soil particles are separated from the slurry, dewatered and returned to the site as cleaned soil. The remaining slurry containing the finer soil portion, coal fines and contaminants are directed to a first stage froth flotation unit where the coal/contaminant fraction is separated from the heavier tailings. Tailings from the first stage are directed to a second stage froth flotation unit where they are combined with waste water from the dewatering of the coarse soil fraction. Tailings from the second stage unit, are removed as clean soil. The coal/contaminant agglomerate produced during froth flotation can be used as a combustible product to offset on-site energy requirements or sold off-site.

A schematic showing the Agloflotation™ process is shown in Figure 3 and described in Alberta Research Council (1990). Treatment costs for a 6 tonne/hour mobile unit are estimated up to $50/tonne depending on availability of coal sources and utilization of coal/contaminant agglomerates (Ignasiak et al, 1989).

The process is capable of cleaning up soil contaminated with coal tar wastes and heavy oils. Treatment of soils contaminated with up to 66 wt % coal tar products showed removal efficiencies of 95 - 100%.

Further investigation is required to determine the treatability of a range of waste feed types and construction and testing of a full scale mobile unit is required.


COAL HOPPER
ROD MILL
CONDITIONING TANK
HIGH SHEAR MIXER
FLOTATION CELLS
LOW SHEAR MIXERS
OIL STORAGE TANK
SOIL HOPPER
TUMBLER
DEWATERING SCREEN
Coarse Soil Product
Fine Soil Product
Middlings
Coal Product

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AGLOFLOTATION$^{T.M.}$ CONTINUOUS PROCESS FLOW DIAGRAM
(Alberta Research Council 1990)

Figure 3

4.4 Low Energy Extraction Process (LEEP)

The low energy extraction process or LEEP is a non-destructive solvent extraction technology currently under development by REMTECH Inc. The process separates contaminants from soils using acetone (for water miscible contaminants) and kerosene (for water immiscible contaminants).

The process consists of six operations: solid-liquid separation, extraction, distillation, liquid-liquid extraction, adsorption and air-stripping.

Contaminated soil feed is separated into liquid and solid fractions by filtration or centrifugation. The solid fraction is transferred to a counter current paddle washer where it is leached with acetone to produce an acetone/water mixture containing organic contaminants and a cleaned soil/acetone slurry. The acetone from the soil/acetone slurry is recovered by steam stripping, and the cleaned soil is discharged as clean fill.

The acetone/water mixture which contains organic contaminants is fed to a counter current centrifugal liquid-liquid extractor containing kerosene and potassium sulphate. The organic contaminants partition into the kerosene producing a contaminated kerosene waste stream, and an acetone/water mixture containing trace levels of contaminants. The contaminated kerosene is sent for disposal while the acetone is recovered from the water mixture by distillation, and the slightly contaminated water is redirected back to the liquid-liquid extractor.

The liquid fraction produced during the initial solid liquid separation stage is passed over an adsorption bed to remove low levels of organic compounds, prior to discharge to the environment. The adsorption bed is redirected back into the contaminated soil stream (Hall et al 1989).

The process schematic is shown in Figure 4.

Bench-scale testing of the LEEP technology has been completed for PCB contaminated sediments and refinery sludges but results were not available.

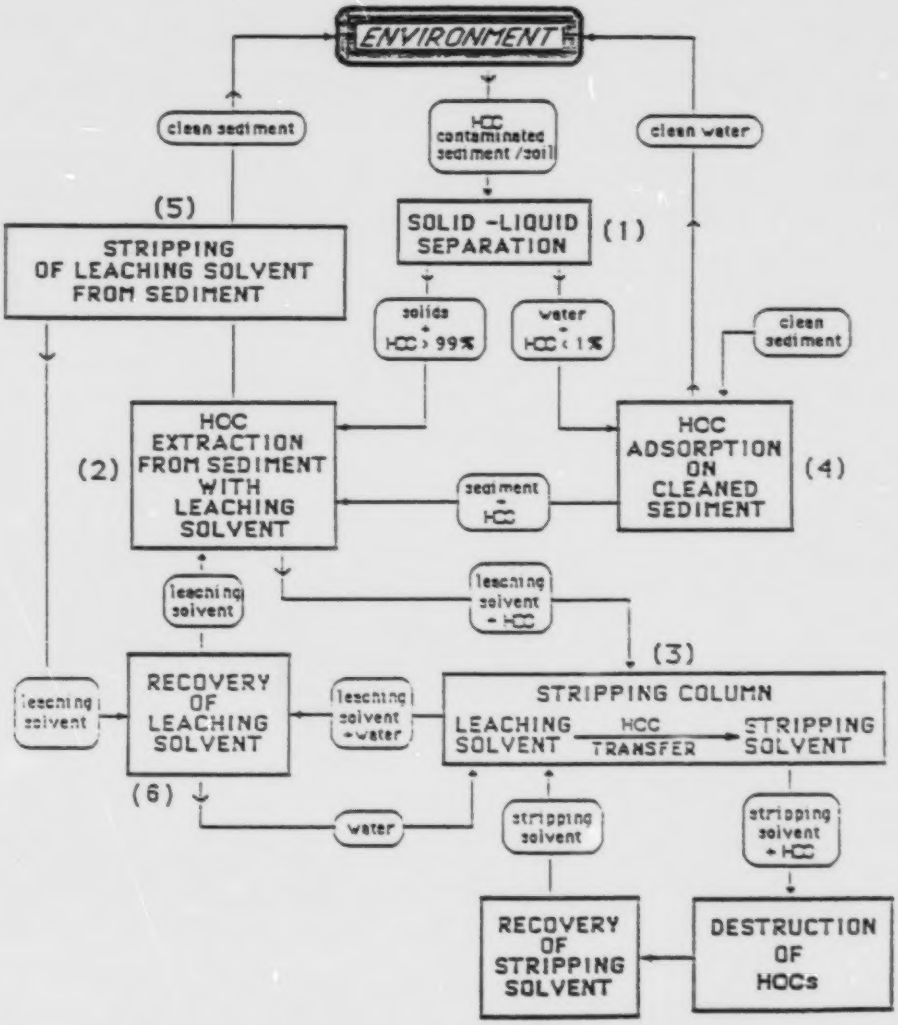
Construction of pilot-scale and full-scale mobile facilities are required to evaluate the technology under field conditions. Further evaluation of the treatability of different waste feeds and contaminant types are required.

4.5 Eco Logic Process

The Eco Logic process utilizes hydrogen at elevated temperatures, to dechlorinate organic compounds and reduce transformation products to end products consisting of hydrogen chloride, ethylene and methane.

Contaminated soil is preheated and injected along with hydrogen into the top of a reactor which is heated to a temperature of 850°C. As the coarse sized material falls through the reactor, organic compounds are volatilized, and the cleaned material is quenched at the base of the reactor. Finer grained soil particles remain entrained in a gas stream within the heated reactor to ensure complete reaction. Most of the waste gas is recycled back into the reactor while a small portion is used as supplementary boiler fuel in the preheating process. A process flow diagram is shown in Figure 5.

The Eco Logic process operates on a continuous mode basis. Capital costs are roughly 5 - 10 times less expensive than incineration and operating costs are 3 - 5 times lower than incineration (Hallett 1990). The process can treat chlorinated organic compounds in a variety of aqueous and solid matrices.


ENVIRONMENT
clean sediment
HCC contaminated sediment /soil
clean water
(5)
STRIPPING OF LEACHING SOLVENT FROM SEDIMENT
SOLID -LIQUID SEPARATION
(1)
solids + HCC > 99%
water + HCC < 1%
clean sediment
HCC EXTRACTION FROM SEDIMENT WITH LEACHING SOLVENT
(2)
sediment + HCC
HCC ADSORPTION ON CLEANED SEDIMENT
(4)
leaching solvent
leaching solvent + HCC
(3)
leaching solvent
RECOVERY OF LEACHING SOLVENT
leaching solvent + water
STRIPPING COLUMN
LEACHING SOLVENT
HCC TRANSFER
STRIPPING SOLVENT
(6)
water
stripping solvent
stripping solvent + HCC
RECOVERY OF STRIPPING SOLVENT
DESTRUCTION OF HOCs

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Revisions	Date

LOW ENERGY EXTRACTION PROCESS (LEEP)
(Applied Remediation Technology, Inc. undated)

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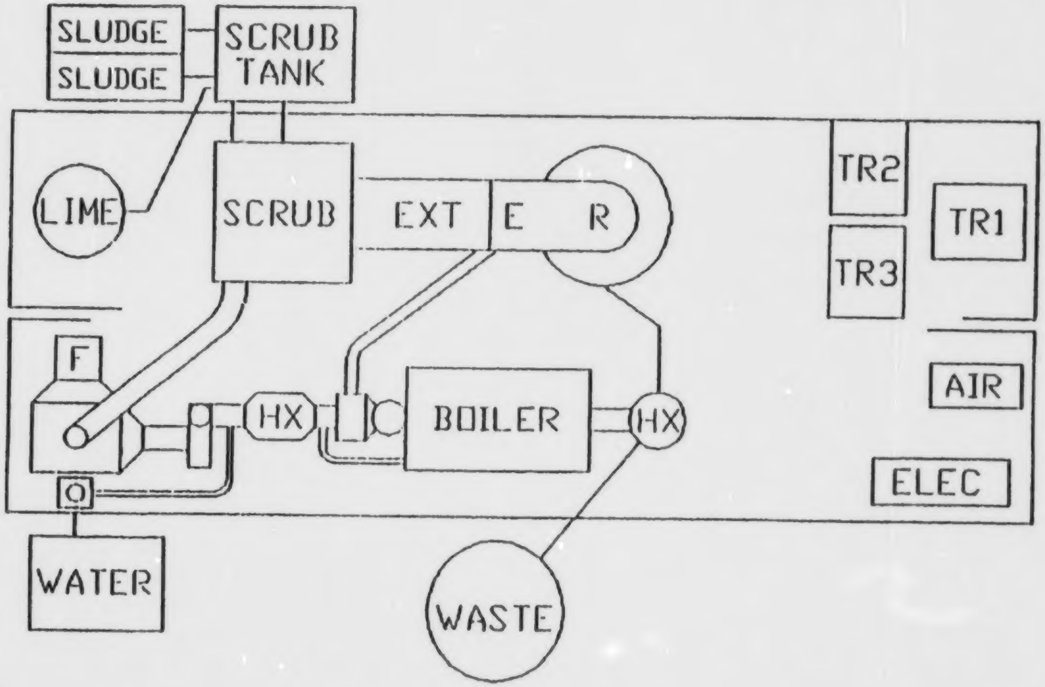
Figure 4


SLUDGE
SLUDGE
SCRUB TANK
LIME
SCRUB
EXT
E
R
TR2
TR1
TR3
F
HX
BOILER
HX
AIR
ELEC
WATER
WASTE

INTERA KENTING

EQUIPMENT LAYOUT FOR ECO LOGIC DECHLORINATION PROCESS
(Hallett et al 1990)

Figure 5

The process has been evaluated at the bench-scale where destruction efficiencies of 99.9999% have been reported (Hallett 1990), but evaluation of pilot-scale and full-scale demonstrations are required. A test program for the Canadian Department of National Defense was proposed for 1990.

4.6 Bioreactors

Bioreactors are an important development in the application of biotechnology to the destruction of organic compounds. Bioreactors offer several advantages over conventional landfarming techniques in the treatment of contaminated soil including:

- operator can maintain greater control of process
- mixing of soil in reactor increases availability of nutrients and contaminants to microorganisms
- biodegradation is faster and more effective
- process can treat complex organic compounds
- process can treat finer grained, clays and sludges

Bioreactors include both vessel or tank type reactors and aeration lagoons. In the case of tank type bioreactors, contaminated soil is screened for size and then directed to the reactor tank where the soil is slurried with water and nutrients, and aerated to maintain optimum conditions for microbial growth. The liquid content of the slurry is maintained at between 80 - 90 wt% (Brox and Hanify 1989). Surfactants may also be added to solubilize the contaminants and improve the availability of the carbon source to the microorganisms.

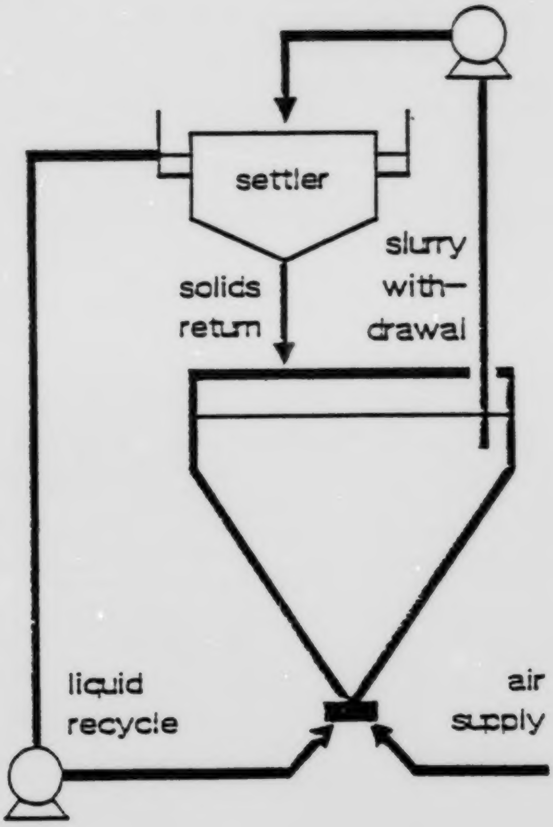
Bioreactors can be operated in batch mode, but continuous reaction is possible with the use of multiple stage reactors. On completion of the treatment, the solids are dewatered by filtration or centrifugation and can be backfilled on-site as clean soils. The liquid effluent from the dewatering process can be redirected back to the mixing tank to slurry the next batch of contaminated soil. Volatile emissions can be treated on line or redirected back into the bioreactor to be biodegraded.

A schematic of a 3-phase slurry bioreactor is shown in Figure 6.

Readily biodegradable organic compounds such as light aliphatic hydrocarbons and low molecular weight PAH's are degraded in bioreactors at rates that are considerably shorter than conventional landfarming. Higher molecular weight PAH's such as benzo(a)pyrene have shown degradation rates of 30% in 14 days (TNO 1988) in laboratory studies.

USEPA (1988) reported degradation rates of up to 95% in 14 days for loamy soils contaminated with up to 6.5% cutting oils, and a ninety percent reduction in dichloromethane within one day at initial concentrations of 20-30ppm in bench and pilot-scale studies in the Netherlands.

At Delft University of Technology in the Netherlands, 70% biodegradation of soil contaminated with diesel fuel at initial concentrations of 10ppm occurred after 200 hours (Kleijntjens 1989). Degradation rates of 60 - 96% for oil and grease from refinery sludges were reported by Brox and Hanify (1989) and Sanexen International (1990). Symons and Sims (1990) reported half lives ranging from 15 - 17 days for fluoranthene and 173 - 231 days for benzo(g,h,i,)perylene in batch reactors. Reductions of 98 - 99% were achieved


settler
slurry
with-
drawal
solids
return
liquid
recycle
air
supply

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PROCESS SCHEMATIC OF 3-PHASE SLURRY BIOREACTOR
(Kleijntjens and Luyben 1988)

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Figure 6

for pentachlorophenol, benzo(a)pyrene, phenanthrene and anthracene in the treatment of contaminated soils and sludges at a wood preserving plant in Tennessee using aeration lagoons (Shack et al 1989).

Further research is continuing into the use of dry bioreactors to eliminate the dewatering process (USEPA 1988) and into methods to optimize biodegradation of organic compounds in a variety of different soils and sludges through the use of temperature control, aeration, addition of acclimated microbes, surfactants, solvents and ultrasound.

Operating costs for treatment using bioreactors has been estimated at $40-$70 per tonne (Brox and Hanify 1989, USEPA 1988).

5. SUMMARY

A literature review of approximately forty-five technologies was undertaken for the on-site clean-up excavated soil contaminated with petroleum hydrocarbons, wood preserving chemicals, and chlorinated solvents. These technologies are in various stages of development ranging from bench-scale through to commercially well developed mobile systems. Although in general the various technologies are well described in the literature, there is a lack of critical third party evaluation of the technologies under field-scale conditions.

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SOLVENT EXTRACTION AND RECOVERY OF PETROLEUM HYDROCARBONS FROM SOIL

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INTRODUCTION

The Emergencies Engineering Division (EED) of Environment Canada is currently comparing the effectiveness of two solvents in terms of their ability to remove petroleum hydrocarbons from soil, as part of a project jointly funded by EED and GASReP. Hexane and natural gas condensate were chosen as the solvents to be investigated because they are inexpensive relative to other solvents and are available at refinery sites, one of the areas where this solvent extraction process is expected to be used.

To date, EED has used a laboratory scale solvent extraction method to compare the two solvents, using three types of soil and a light crude oil to create simulated contaminated soils. These soils and solvents have also been used to optimize the mixing portion of the bench scale extraction process.

The next stage of the evaluation is to set up a bench scale system which will use the simulated contaminated soils, as well as actual contaminated soils, to further evaluate the solvent extraction process. Upon successful completion of the lab and bench scale investigations, a mobile solvent extraction unit will be constructed for use at contaminated soil sites.

BACKGROUND

In 1988, EED was given a sample of diesel invert drilling muds (DIDM) by Gulf Canada Ltd. and was asked to investigate methods of removing the oil from the shale in the sample. A solvent extraction method using hexane was examined. The process involved mixing hexane with the muds, decanting the liquid and centrifuging the remaining slurry. The recovered liquid from the mixing and centrifuge stage was distilled to separate the hexane from the oil extracted. The results obtained using this method were favourable, with approximately 80% solvent recovery and the production of a dry shale with no detectable petroleum odour.

Approximately a year after the DIDM tests were performed, EED became involved in the GASReP program and put forth a proposal to investigate the use of solvent extraction as a method of removing petroleum hydrocarbons from soil. Solvent extraction is a technology which has been used effectively in industry for several decades, but it has only been recently that the technology has been used in the soil remediation field. Many of the existing units use proprietary solvents. It is these types of solvents which in many cases make the process expensive. (Raghavan et al, 1989)

The original intent was to study hexane as a solvent, but it was suggested that natural gas condensate (NGC) should also be used as a possible solvent. NGC was recommended for this process because a significant number of the compounds found in the NGC are considered solvents for petroleum hydrocarbons. NGC is also a low-demand product of the petroleum refining process making it inexpensive in comparison with pure solvents.

Figure I shows a schematic of the proposed solvent extraction process. The process involves mixing the contaminated soil, in a mixing chamber, and then allowing the mixture to settle. Once settled, the free liquid is decanted. The slurry is sent to a centrifuge where the majority of the remaining liquid is removed.

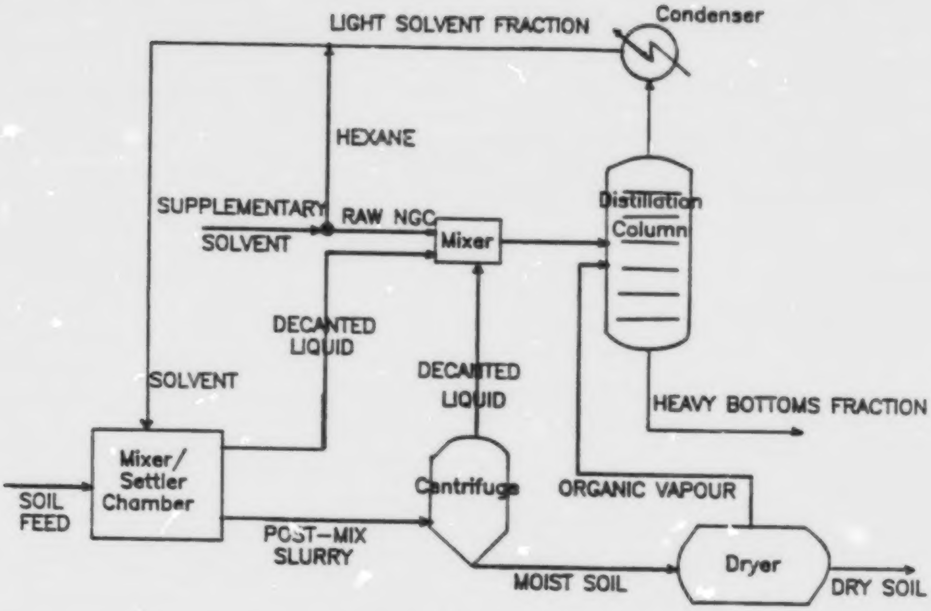
LIGHT SOLVENT FRACTION
Condenser
HEXANE
SUPPLEMENTARY
SOLVENT
RAW NGC
Mixer
Distillation Column
DECANTED LIQUID
SOLVENT
DECANTED LIQUID
HEAVY BOTTOMS FRACTION
SOIL FEED
Mixer/ Settler Chamber
Centrifuge
ORGANIC VAPOUR
POST-MIX SLURRY
Dryer
MOIST SOIL
DRY SOIL

FIGURE 1: PROPOSED SOLVENT EXTRACTION PROCESS FOR RECOVERY OF HYDROCARBONS FROM SOIL

The liquid collected from the mixing and the centrifuge stage is fed to a distillation column where the solvent fraction (light ends) is removed and returned to the mixing stage. The heavy bottoms fraction can be sent back into a refining process for further treatment. The soil removed from the centrifugal stage is sent to a dryer to remove any further organic compounds. The organic vapour from the drying stage can be fed into the distillation column as supplementary feed.

In the case were NGC is used, the raw condensate mixture will have to be pre-distilled in order to produce a useable solvent. In Figure 1, the schematic shows the possibility of mixing the raw NGC with the decanted liquid stream to form the feed to the distillation column. This will allow the NGC to be pre-distilled and only the solvent fraction of the NGC to be sent to the mixing chamber. A further sizing and costing investigation is required in order to determine whether it is feasible to use one column for both solvent recovery and pre-distillation of the NGC. The results of this costing study and the results of the laboratory work performed by EED will help determine the overall feasibility of using NGC as a solvent in this process.

MATERIALS

Soils

For the lab-scale portion of the tests, three types of soils were used, a sandy soil, a high organic soil and a silty/clay soil. For simplicity these soils will be named *sand*, *peat* and clay respectively. Table 1 shows the results of the mechanical analysis performed on the soils. The percent moisture analysis was performed in house by EED. The Wastes and Chemicals Division of Alberta Environment performed the remaining mechanical analysis for the sand and peat. The Geological Survey of Canada performed the particle size distribution for the clay.

TABLE 1: SOIL MECHANICAL ANALYSIS

SAMPLE	PEAT	SAND	CLAY
$CaCl_2$ pH	4.88	5.07	NA
% TOTAL CARBON[1]	11.6	0.84	NA
% $CaCO_2$	<0.7	<0.7	NA
Loss on Ignition at 420°C	26.85	2.08	NA
% SAND[2]	85.6	86.4	0.5
% SILT	11.2	6.4	14.9
% CLAY	3.2	7.2	84.5
Texture	loamy sand	loamy sand	NA
Average % Moisture(wt)	54.3	9.0	35.2

NOTES:
1. Organic Carbon = %Total Carbon - %$CaCO_3$
2. The values for percent sand, peat and clay are the percent of total inorganic particles in the soil samples.

Solvents

Solvent grade hexane (98%) was used for the hexane solvent extraction runs.

One barrel of natural gas condensate was donated to EED by Parklands Refinery Limited of Bowden, Alberta. Table 2 shows the approximate weight percentages of the various components contained in a condensate similar to the condensate received. The mass fractions and boiling ranges shown are for a Mobile Harmattan area gas plant condensate based on analysis performed by Core Laboratories of Alberta on May 9, 1990. Figure 2 shows the percent of light ends recovered at specific distillation temperature cutoff according to EED's distillation results.

Petroleum Hydrocarbons

The oils to be used to contaminate the soil samples were a light crude oil, a diesel and a bunker C. The crude oil was obtained from an Esso Petroleum site near Sarnia, Ontario. The diesel and bunker C are being obtained locally.

Only the light crude oil has been used in the tests performed to date. Once the pilot scale process has been assembled the bunker C and diesel oil as well as the crude oil, will be incorporated in the test protocol.

TABLE 2: COMPOSITION OF PARKLAND'S NATURAL GAS CONDENSATE

COMPOUND	MASS FRACTION	BOILING POINT RANGES (^{o}C)
Hexanes	0.138	36.1 - 68.9
Heptanes	0.089	68.9 - 98.3
Octanes	0.070	98.3 -125.6
Nonanes	0.040	125.6 -150.6
Decanes	0.046	150.6 -173.9
>Decanes	0.139	173.9 plus
Cyclopentane	0.001	48.9
Methylcyclopentane	0.021	72.2
Benzene	0.016	80.0
Cyclohexane	0.016	81.1
Methylcyclohexane	0.027	101.1
Toluene	0.037	110.6
Ethylbenzene,p+m-Xylene	0.036	136.1 -138.9
o-Xylene	0.008	144.4
1,2,4 Trimethylbenzene	0.009	168.9
TOTAL[1]	0.693	

NOTE: 1. Remaining portion of mass fraction is composed of unclassified compounds

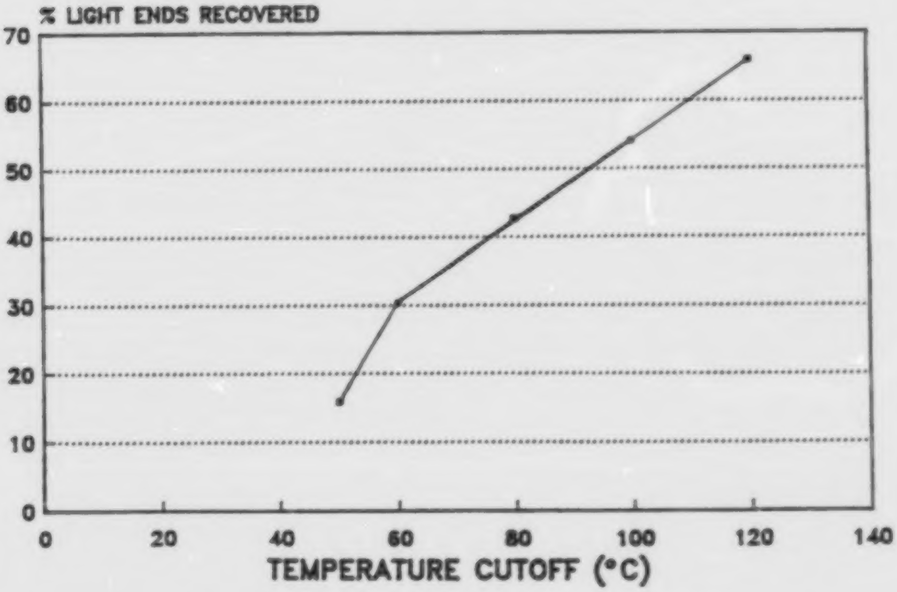

FIGURE 2: PARKLANDS NATURAL GAS CONDENSATE - TOTAL PERCENT LIGHT ENDS RECOVERY VERSUS TEMPERATURE CUTOFF

METHODS

Solvent Extraction Comparison Method

In order for a rough comparison to be made between hexane and NGC as solvents for removing oil from soil, a simple solvent extraction method was used so that several tests could be performed in a short period of time.

Because of initial difficulties in determining the transport of the water during the extraction process, all moisture was removed from the soil during this stage of the testing. For this method the soil was dried in an oven. The soil was then placed in a fleaker and was contaminated with the oil using a pipette. The fleaker was capped and let stand in a fumehood, for 24 hours, to allow the oil to absorb into the soil. The fleaker was re-weighed in order to account for any loss of volatile compounds.

The desired amount of solvent was added to the fleaker and the fleaker was shaken by hand for one minute. The soil was then allowed to settle for 30 minutes. The extracted liquid was decanted into a boiling flask and attached to the distillation apparatus as shown in Figure 3. The extracted liquid was then distilled in order to collect the pure solvent in the top flask. The boiling cut-off (ie. temperature at top of reflux condenser) for the hexane was 68°C and whereas the cut-off for NGC was 86°C. The recovered soils were dried in an oven, at 90_{o}C, in order to drive off any excess volatiles.

The NGC was pre-distilled during these tests so that the fraction used as the solvent was the liquid collected from the boiling range between 50°C and 80°C. It was found that this distillation fraction made up approximately 26% of the NGC sample (see in Figure 2). In the remainder of this paper when NGC is mentioned it is this 26% fraction which is being referred to.

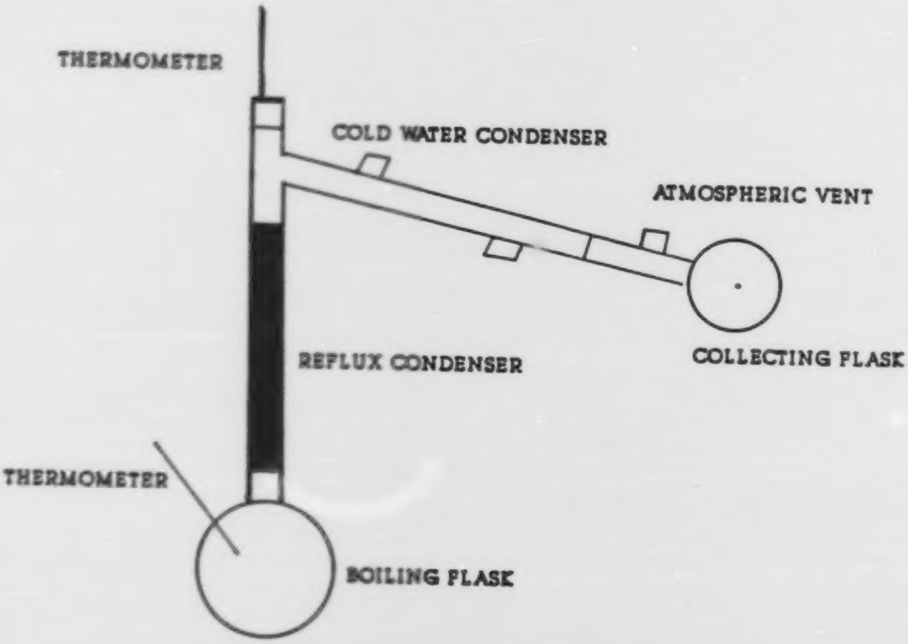

FIGURE 3: DISTILLATION APPARATUS

The following variables were tested during this stage of the experimentation:

- Soil type: sand, peat, clay;
- Oil type: Ontario light crude;
- Solvent type: hexane, natural gas condensate;
- Percent oil contamination: 0%,1%,3%,5% and 10% (wt oil/wt soil);
- Number of extractions: one;

and,

- Ratio of solvent to soil mixture: 1:1,2:1 and 3:1 (by weight).

Method With Ball Mill

The next stage of testing involved the optimization of the mixing stage of the process. In order to mix the solvent and contaminated soils thoroughly and consistently a ball mill was used. At this point, the method for contaminating the soils was altered. The new method involved retaining the moisture in the soil. The new method involved placing approximately four centimeters of soil in a 12cm by 12cm perforated tray. The weight of the soil in the tray was determined. Oil was added to the soil until the oil seeped out the perforations so that the final percent of oil contamination would be the saturation limit of the soil (usually 20% for the sandy soil). The tray was then allowed to sit in the fume hood. After 16 hours the pan was re-weighed in order to determine the final amount of oil in the soil.

Approximately 200g of contaminated soil and the desired amount of solvent were added to the ball mill jar. The ball mill was run at the desired speed for the desired mixing time. The solvent layer was then decanted and distilled using the same procedure as in the solvent comparison method.

The following variables were tested during this stage of the experimentation:

- Soil types: sand;
- Oil type: Ontario light crude oil;
- Solvent type: hexane;
- Ball mill speed: (30%, 60%, 75% and 90%) (31rpm, 49rpm, 58rpm and 67rpm);
- Ball mill mixing time: 30s, 60s, 180s
- Percent oil contamination: saturation (approx. 20wt%)
- Total solvent to soil ratio: 2:1
- Number of extraction: 3 (ie. 3 times 2:3 solvent/soil) 4 (ie. 4 times 1:2 solvent/soil)

Alternative Soil Contamination Method

Because it was difficult to determine whether the losses during the 16 hour sitting period were due to volatilization of oil or to evaporation of water, another method for contaminating the soils is being investigated at this time. This method involves weathering the oil in an open stirred container over 16 hours and then adding this oil to the soil. It has been found that stirring this specific oil for greater than 16 hours resulted in no further loss of volatiles, so that it can be assumed that there will not be any further volatile loss once this weathered oil is added to the soil.

Analytical Methods

Up until this point in the testing most of the analytical work has been gravimetric. In order to perform a complete mass balance on the system, mass measurements were taken after each step in the extraction process, but because it was difficult to trace the path of the water and the volatiles in the system other analytical methods are being studied. The extracted liquids, before and after distillation are being analyzed using gas chromatographic/flame ionization detection (GC/FID) methods and UV spectrophotometric methods.

The GC/FID methods gave some indication of the composition, in terms of light and heavy ends, of the liquid extracted from the soils. As well, the GC/FID was used to determine the purity of the distilled solvent. The UV spectrophotometry method was set up to determine the percent of oil in the extracted liquid. This was done by creating standard solutions of oil in solvent and producing calibration curves using various wavelengths.

A freon extraction method will be used in the future to evaluate the oil and solvent composition of the recovered soils.

RESULTS

During the solvent comparison tests, several runs were performed where uncontaminated soil was shaken with solvent, in order to determine the amount of solvent which will remain in the soil during the extraction process. These residual amounts will vary with varying quantities of oil in the soil, but the numbers obtained from these runs gave an indication of the behaviour of the solvent in terms of soil type and amounts of solvent initially added. Table 3 shows the solvent residual results for the runs using a solvent to oil ratio of two and three. The percent of solvent residual was determined by drying the recovered soils, at 90_oC, and comparing the weight of the dried soil to the weight of the original soil sample used. The freon extraction analysis will give a better indication of the residual solvents in the soils.

TABLE 3: SOLVENT TYPE AND QUANTITY VERSUS SOLVENT RESIDUE

SOIL TYPE	SOLVENT TYPE	SOLVENT/SOIL RATIO (WT)	SOLVENT RESIDUE % WT SOLVENT/SOIL
sand	hexane	2:1	0.12
		3:1	0.18
	NGC	2:1	0.00
		3:1	0.05
peat	hexane	2:1	0.17
		3:1	0.24
	NGC	2:1	1.94
		3:1	1.89
clay	hexane	2:1	0.23
		3:1	0.19
	NGC	2:1	0.79
		3:1	0.64

The above numbers do not take into account any removal of organics naturally found in the soils. A GC/FID analysis was performed on the decanted hexane, after mixing with un-contaminated soil, to determine if any organic constituents originally in the soil were removed by the solvent. The chromatograph, of hexane decanted from uncontaminated sand, showed only hexane to be present. The hexane removed from the uncontaminated peat soil was coloured. A GC/FID analysis has not yet been performed on these samples, but this colour change would indicate the removal of organics originally found in the peat. This removal of organics will further complicate the calculations of the mass balances.

Figure 4 shows the percent of oil recovered in terms of solvent type, soil type, percent oil contamination and solvent to soil ratio. The oil recovery percents shown in these graphs were

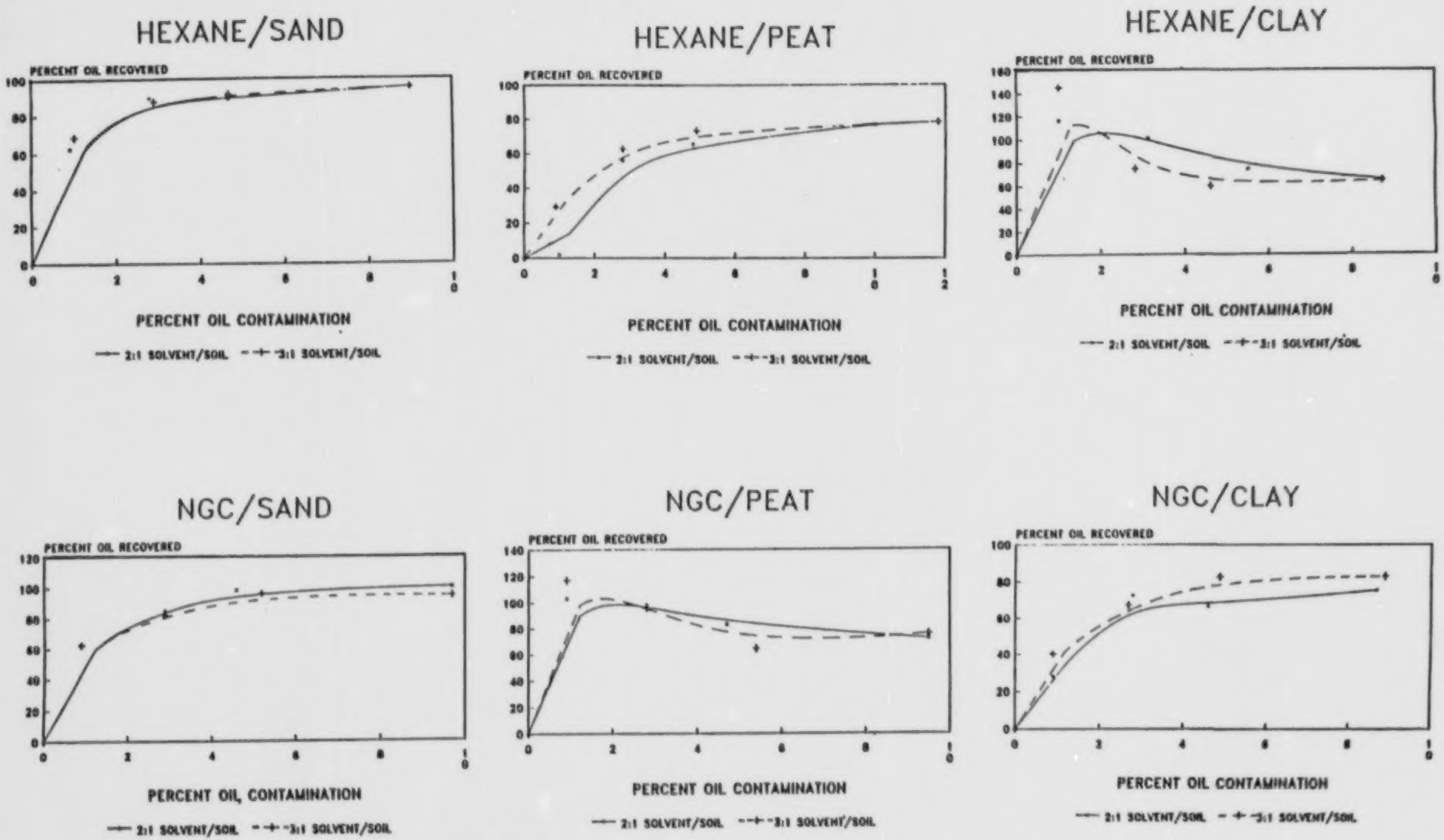

FIGURE 4 - EFFECT OF SOLVENT TYPE AND SOLVENT/SOIL RATIOS ON OIL RECOVERY PERCENTAGES

calculated by dividing the mass of the heavy distillation fraction by the mass of oil in the soil at the time the solvent was added. It should be assumed that in all cases these numbers are slightly high because the heavy distillation fraction contained some suspended solids and organics originating in the soil especially the peat. For this reason these numbers should only be used for comparison purposes and not actual removal quantities.

During the ball mill optimization tests, the soils to be contaminated were not dried and therefore the water originally found in the sample had to be incorporated in the mass balance on the system. During these tests it was observed that the decanted liquid from the mixing was homogeneous. Since this liquid is hydrophobic it can be assumed that the water originally in the soil samples is either remaining in the soil or is partially evaporating during the sample settling time.

Several runs were performed with the ball mill, altering the mixing speeds and mixing times. The gravimetric results obtained from these runs did not show a significant difference in oil recoveries when the mixing speeds and mixing times where altered. UV spectrophotometric analysis were performed on a few of the extracted liquids obtained using the various ball mill parameters. Figure 5 shows the average UV spectrophotometric results for 3 separate ball mill runs. Each run used a 20% contaminated sand and 3 extractions using a 2/3 solvent to soil ratio.

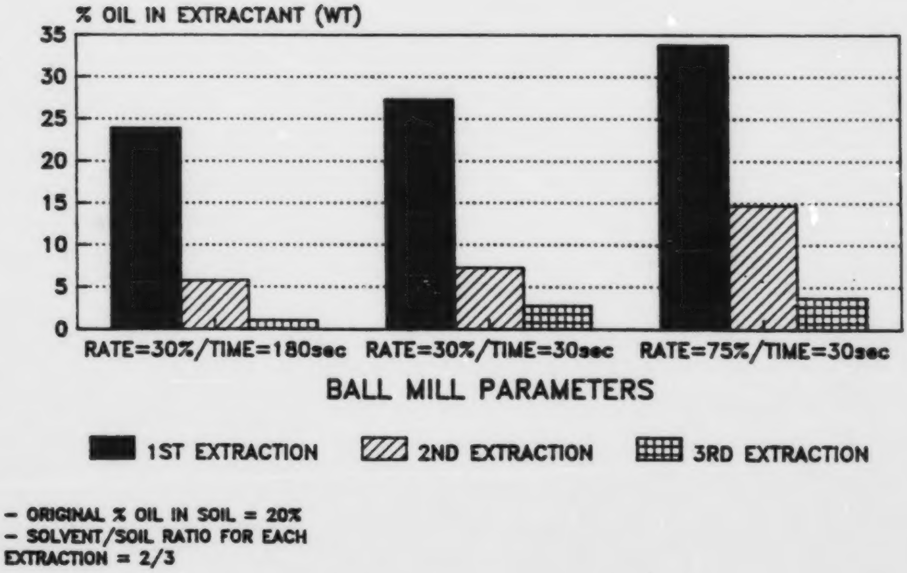

FIGURE 5: AVERAGE UV SPECTROPHOTOMETRIC RESULTS FOR VARIOUS BALL MILL MIXING RATES AND TIMES

DISCUSSION OF RESULTS

Table 3 and Figure 4 can be used to compare the effects of using hexane with NGC as solvents. Table 3 shows that, in terms of solvent residual, the sandy soil retains more hexane than NGC, but clay and peat both retain a greater percent of NGC. Peat retains the greatest amount of solvent, with a residual of almost 2% NGC/soil (wt/wt). Since NGC contains heavier compounds than the hexane these results show that sandy soil will retain light ends better than heavy ends and that clay and peat will retain heavy ends better than light ends. In the pilot scale process the separation will be performed using a centrifuge which should greatly reduce the residue solvent quantities in the soils, but the above results give a relative idea of the interactive behaviour between the solvents and the soil types. Again, because the amount of organics removed from the peat, is not known, it is difficult to compare peat residual amounts with the sand and clay residual amounts.

In Figure 4 it can be seen that, for a specific oil contamination percent, hexane and NGC each recover approximately the same percent of oil from the sand. At oil contaminations of less than 3% the NGC removes a greater quantity of oil, than hexane does, from the peat. At greater than 3% contamination, the percent of oil removed from the peat becomes similar for hexane and NGC. The opposite seems to be true for the clay where the hexane removes more oil from the clay soil with less than 3% oil contamination. Again the results for removal of oil from the clay at oil contamination greater than 3% gave similar results for the two solvents.

Figure 4 also shows that the greater the initial oil contamination is, the greater the percent of oil recovery is, in all cases except the hexane/clay combination and the NGC/peat combination.

According to Figure 4, when either hexane or NGC is being used with sand there is no significant difference between using a solvent to soil ratio of two or three. For the hexane/peat combination and NGC /clay combination, the solvent to soil ratio of three gave greater percent oil recoveries than the solvent to soil ratio of two. The hexane/clay and NGC/peat combinations showed higher percent oil recoveries for the ratio of three than for the ratio of two at oil contamination of about 1% but the ratio of two gave higher percent oil recoveries at oil contaminations greater than 2% by weight. In the cases where the percent oil recoveries are higher for the ratio of three, the increase that occurs, in all cases, is less than 20% and therefore it would be uneconomical to add 50% more solvent in order to remove additional 20% of oil.

In comparing the residual solvent results shown in Table 3 it can be seen that there is not any significant difference in the amount of residue solvent when using a solvent to soil ratio of two as opposed to a ratio of three. For economic reasons and using the above findings a solvent to soil ratio two would be sufficient for this process.

As stated in the results section the gravimetric ball mill results basically show that the mixing rates and mixing times do not have a significant effect on the amount of oil recovered, but when examining the UV spectrophotometric results in Figure 4 one can see a trend. At a high mixing rate of 75% (67rpm) and a low mixing time of 30sec the percent of oil in the extracted liquid is greater than at lower mixing rates and higher mixing times.

Because of delays in receiving various pieces of equipment and the limited analysis performed on the samples from the tests completed to date. The data and the calculated results shown should only be taken as approximations of the results expected from the actual bench scale system.

FUTURE WORK

The next stage of this project is to continue to optimize the remaining sections of the bench scale process. This will include the centrifuge and the distillation processes. Once the bench scale is constructed, the comparison testing of the hexane and the NGC will continue using the simulated contaminated soil samples, as well as actual contaminated soil samples. The sample sizes used in the bench scale process will be approximately 4 times that of the laboratory scale process. More work will be performed comparing the solvent extraction abilities of various distillation fractions of the NGC. Petroleum products, besides light crude oil, will also be used to contaminate the soil samples.

The effect of solvent to soil ratio and number of extractions will continue to be evaluated in order to help determine the most cost effective method of using the solvents.

The analytical methods needed to fully analyze the recovered liquids and soils will be developed. The EED laboratory is currently being set up to test the recovered soils using freon extraction methods.

CONCLUSIONS

The evaluations performed to date on the proposed solvent extraction process show that both the natural gas condensate distillate fraction and hexane are effective as solvents for removing oil from contaminated soil and that neither of the solvents have proven to be significantly better than the other. For sandy soil there is no apparent difference between using hexane or NGC in terms of the percent recovery of oil from the soil, but it seems that the sandy soil will retain more hexane than NGC. At oil contamination percentages of greater than 3% the results have also shown no difference between using hexane or NGC in the percent recovery of oil for the peat and clay soils. At oil contaminations of less than 1%, NGC will remove more oil from peat than hexane but at these contamination levels hexane will remove more oil from clay than NGC. Both peat and clay will retain more NGC than hexane.

The results also show that when using hexane or NGC as a solvent it is not feasible to use a solvent to soil ratio of greater than two because the increase amount oil removed, if any, is not significant.

It was found that when mixing the soils with the solvent a high mixing speed for a short period of time results in the greatest oil recoveries.

During the next stage of the project the bench scale process will be assembled and the parameters tested during the laboratory scale portion of the project will be re-evaluated using the bench scale system.

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January 15, 1991

A SURFACE BIOREACTOR FOR CLEANING HYDROCARON AND SALT CONTAMINATED SOILS AND SLUDGES

by

Lin T.L. Callow

Gulf Canada Resources Limited

Introduction

Gulf Canada Resources Limited in it's ongoing efforts to provide proper management of it's wastes produced from oilfield operation, has designed and conducted preliminary tests of a "surface bioreactor". This bioreactor design utilizes the processes of biodegradation and leaching to remove the hydrocarbon and salt contamination found in many oil and gas field wastes.

Gulf is currently working with the University of Calgary, the Alberta Environmental Centre, Envirotest Labs, the Alberta Environmental Research Trust, the Environmental Research Advisory Council of the Canadian Petroleum Association and Environment Canada to optimize the treatments and design prior to field testing a near operational scale bioreactor unit.

Conventional landfarms provide a cost effective option for treating hydrocarbon contaminated solids, however, no cost effective method of treating solids contaminated with hydrocarbon and salts is currently available. Due to high salt and hydrocarbon levels this material cannot be safely landfilled or landfarmed and other high tech approaches are either too expensive or incapable of treating the salts or the hydrocarbon contaminants.

Based on Gulf's experience several types of candidate contaminated materials for bioreactor treatment are created by the Petroleum Industry in relatively large volumes. Of these materials the following are being considered as research candidates:

1) hydrocarbon and salt contaminated soils from spill sites and seepage from flare pits and other containment structures

2) diesel invert based drilling mud cuttings and contaminated soils

3) soils and sludges contaminated by high asphaltene content heavy oil wastes, salts and/or heavy metals

4) gasoline, diesel fuel, lube oil or light hydrocarbon contaminated soil material from spills or tank leakages.

Design Concept

The surface bioreactor design consists of an intensive biological treatment and leaching system contained within a synthetically lined dike structure. The design allows for amendment and nutrient additions, aeration, irrigation, leachate collection, monitoring and collection of volatile organics and waste heat utilization.

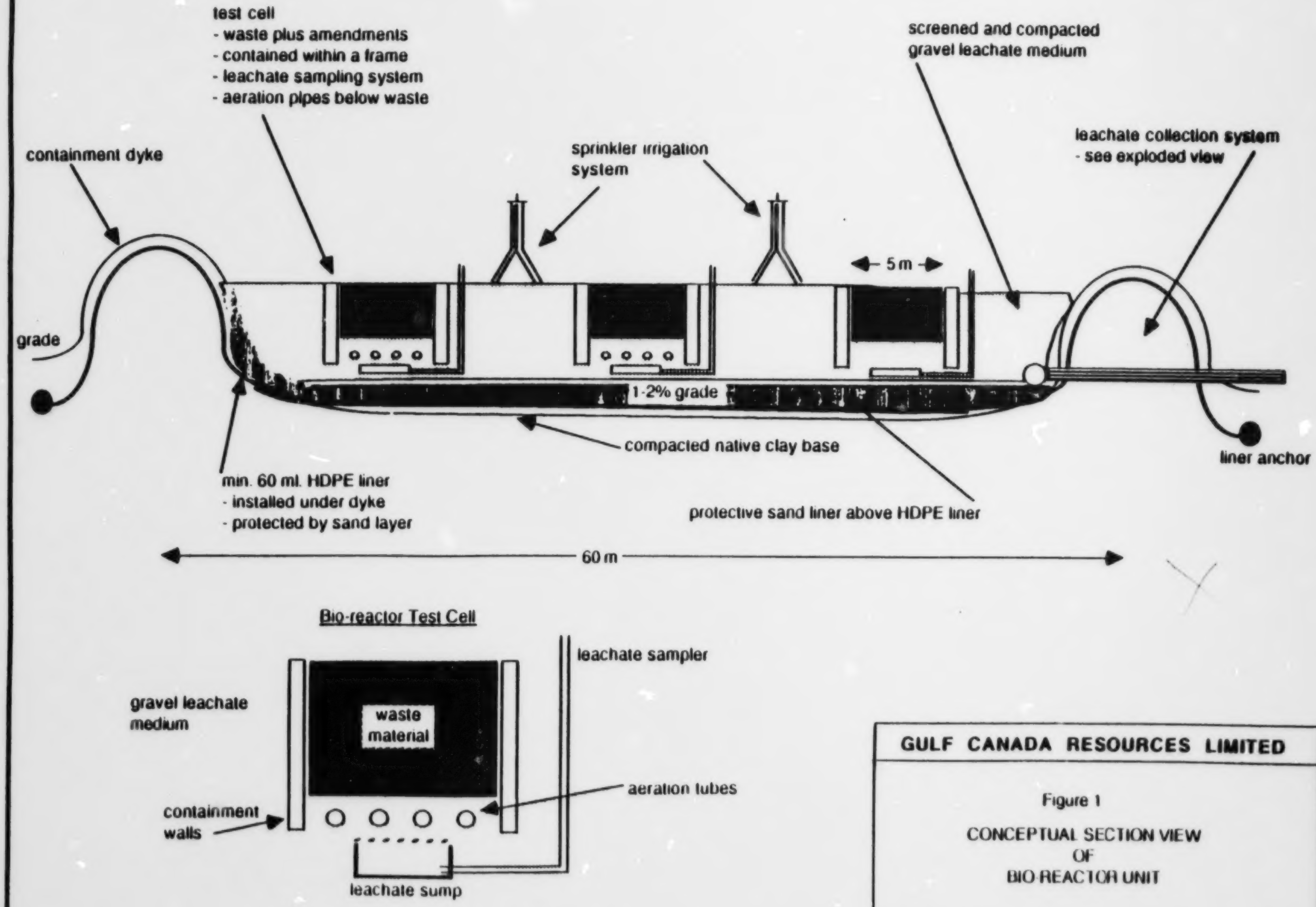
Figure 1 is a cross-sectional schematic drawing of one of the two treatment units that are proposed for this project. One bioreactor will initially be used to test the engineering design with a simple waste; the second unit will test other wastes and/or alternate treatment regimes based upon laboratory scale experiments.

Each entire biological treatment unit will be underlain by a synthetic liner placed over natural compacted clay to prevent groundwater contamination. A thin sand layer will be placed on top of the synthetic liner to protect it. A screened and compacted gravel layer will be installed above the sand layer and nine contained test cells will be installed within this gravel year. The contaminated materials will be placed on this gravel layer for treatment.

There are two types of leachate collection systems proposed. The main system is located at the down-slope end of the biological treatment unit and consists of a perforated tile drainage pipe connected to an external sump. The details of the main leachate collection system design are shown in Figure 2. In addition to the main leachage collection system each test cell will have a small leachate sampling system installed immediately under it.

In order to allow a comparison of the effectiveness of tillage versus forced (mechanical) aeration, three of the test cells in each treatment unit will have subsurface aeration systems installed (Figure 1). The forced aeration cells will have perforated or slotted pipe installed in the gravel immediately below the hydrocarbon contaminated material. If feasible waste heat will be utilized in the aeration system. This system is intended to eliminate the need for labour intensive frequent cultivation and to extend the operating season. Three other test cells will be cultivated weekly and three cells will be cultivated monthly for comparison.

The system will be designed to allow for spray irrigation of the land treatment unit using either a fresh water supply or by recirculating water from the main leachage collection sump. A common irrigation rate will be used for the entire site unless moisture and/or leaching rate is a desired variable. Each cell could be irrigated individually if a unit contained both high salt or other high solubility contaminants.



test cell
- waste plus amendments
- contained within a frame
- leachate sampling system
- aeration pipes below waste
screened and compacted
gravel leachate medium
containment dyke
sprinkler irrigation
system
leachate collection system
- see exploded view
5 m
grade
1-2% grade
compacted native clay base
liner anchor
min. 60 ml. HDPE liner
- installed under dyke
- protected by sand layer
protective sand liner above HDPE liner
60 m
Bio-reactor Test Cell
leachate sampler
gravel leachate
medium
waste
material
aeration tubes
containment
walls
leachate sump

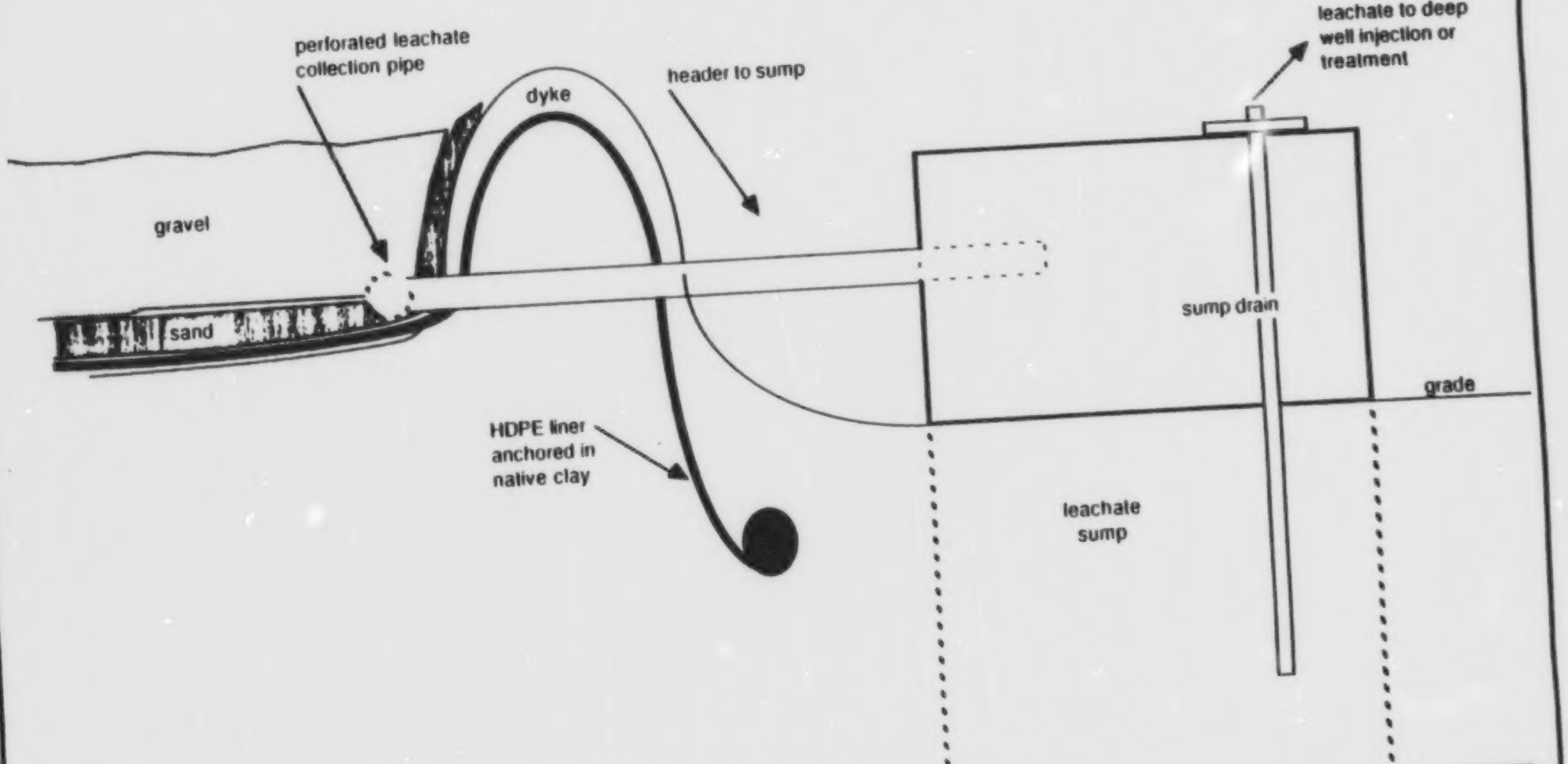
GULF CANADA RESOURCES LIMITED

Figure 1

CONCEPTUAL SECTION VIEW
OF
BIO-REACTOR UNIT

Not To Scale 14/06/90

KBL LAND USE CONSULTING LTD.


perforated leachate collection pipe
dyke
header to sump
leachate to deep well injection or treatment
gravel
sand
sump drain
grade
HDPE liner anchored in native clay
leachate sump

GULF CANADA RESOURCES LIMITED

Figure 2

CONCEPTUAL SECTION VIEW
OF
LINER ANCHOR AND LEACHATE
COLLECTION SYSTEM

Not To Scale

22/08/90

KBL LAND USE CONSULTING LTD.

The main leachate collection sump will be connected to a deep injection well system for disposal of untreatable contaminated water. Alternatively, the main leachate collection system could be connected to a water treatment system, however, this would add considerably to the overall cost. The individual cell leachate sampling system is intended to provide data on the quality of the leachate from each test cell. Salts, metals and target water soluble organic contaminant levels will be monitored. The total volume of leachate will be monitored in the main collection sump.

It is anticipated that vapor monitoring will be conducted to determine the amount of VOC emissions being produced from the treatment cells. This would only be necessary with certain organic contaminants.

If the summer season is too short to allow for acceptable levels of biodegradation within a single year, consideration will be given to covering the units with a plastic greenhouse cover to maintain high substrate temperatures. Waste heat may also be used to extend the operating season. The greenhouse concept would also allow for the inclusion of an emission vapour recovery system if air pollution develops into a significant concern.

Primary Experimental Design

The proposed design of a Bio-Reactor unit is given in Figure 3. The size of the project can be scaled up to include additional units to accommodate the number of individual waste types which can be tested at any one time or to test multiple degradation enhancement techniques. Each unit will consist of nine cells which allow for three replicates of each of three treatments. Replication is a necessary component of a statistically valid design, especially if the waste is heterogenous or difficult to mix uniformly with soil carriers or amendments. Oily waste sludges are in this group and are notorious for the difficulties in handling in field experiments. If wastes to be tested can be applied in a consistent and uniform manner, each of the nine cells could contain a separate treatment but at the cost of a truly replicated design. The non-replicated nine treatment design would constitute demonstration plots and be useful where clear and dramatically different results are anticipated.

For the example given in Figure 3 for testing cultivation/aeration techniques, a replicated design is proposed using minimal cultivation (once per month) throughout, forced aeration and aeration with waste heat added. The depth of waste to be placed in each treatment cell will be 16 cm, the effective cultivation depth. The volume of waste per cell would then be 4 m^3 or about 5.6 tonne per cell (assuming a bulk density of 1.4). The units will be located near an operating facility with a deep injection well and a high volume source of fresh water.

In the case of oily sludges that are liquid or semisolid in nature "carriers" or amendments must be selected and tested. These should be evaluated for efficacy as the type of carrier (soil) has been shown to have major effects on biodegradation

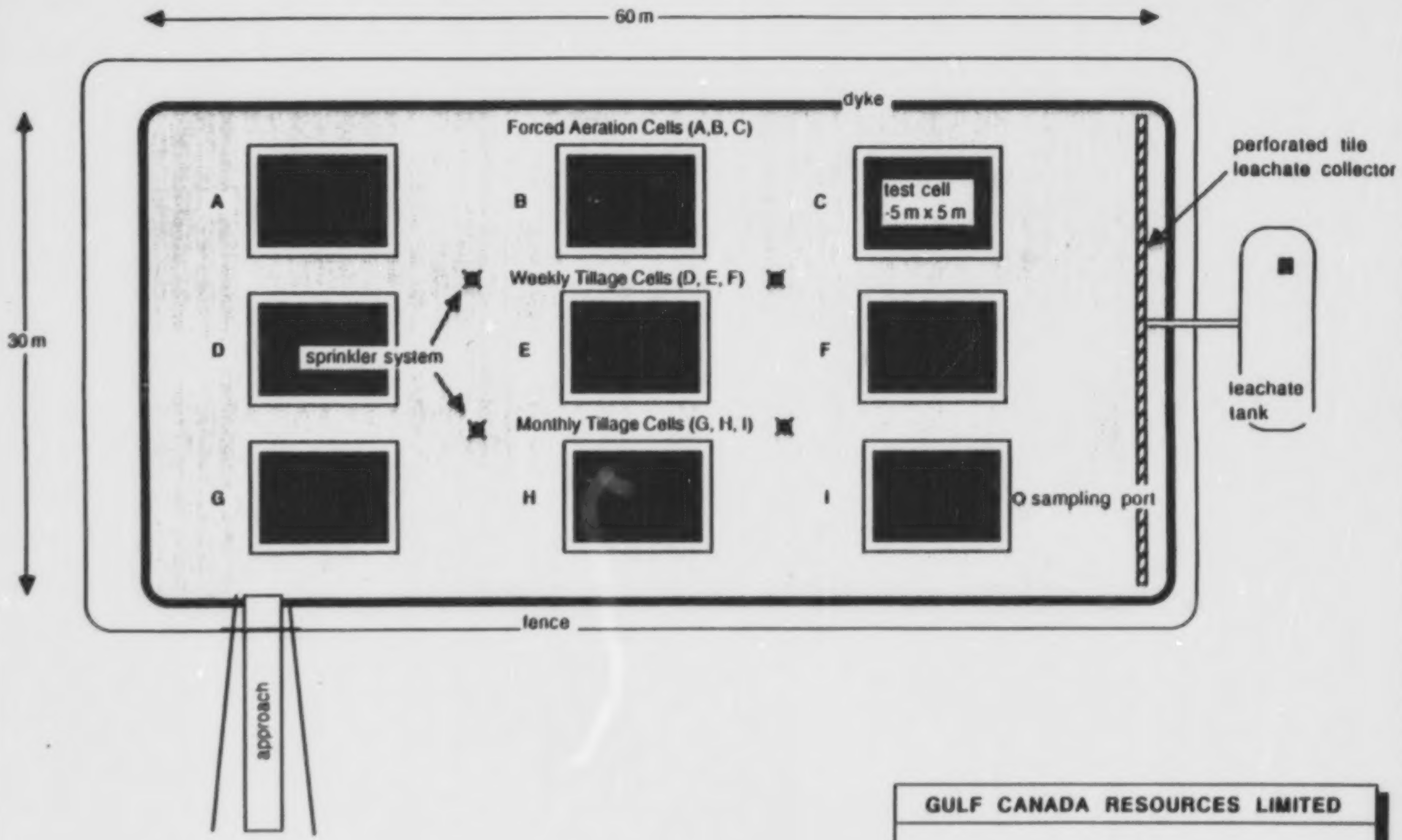

60 m
30 m
dyke
Forced Aeration Cells (A,B, C)
A
B
C
test cell
·5 m x 5 m
Weekly Tillage Cells (D, E, F)
D
sprinkler system
E
F
Monthly Tillage Cells (G, H, I)
G
H
I
O sampling port
perforated tile
leachate collector
leachate
tank
fence
approach

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Figure 3

CONCEPTUAL PLAN VIEW
OF
BIO-REACTOR UNIT
SHOWING TEST CELL LAYOUT

Not To Scale 22/08/90

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rates of hydrocarbon wastes under laboratory conditions (Visser et al. 1987). These materials might include soil, subsoil, sand, spend mushroom compost and green manure amended soil. Coarse woody wastes (sawdust, woodchips) might be incorporated as a physical carrier of toxic organic wastes and as an aeration enhancer.

The analytical protocol has not been developed yet, however, the contaminated materials will be subjected to a leachate analysis both prior and post treatment. The test material will be considered to be cleaned once it is safe for either landfilling in an unlined landfill or for use as a landfill cover material. If topsoil is being treated consideration will be given to cleaning the soil to the point where it can safely support vegetation growth.

Supplemental Treatments

Additionally, all test cells would receive some standard treatments, such as neutralization with calcium carbonate if necessary, fertilization, and amendment with calcium nitrate for high salt content materials.

The test cells will be irrigated and cultivated on a frequent basis in order to optimize both leaching of salts and biodegradation of the hydrocarbon. It is expected the irrigation rate will be relatively high and a calcium source (e.g. calcium nitrate) will be added in the initial treatment period, until salt levels have been reduced to the point where they will no longer interfere with biodegradation. Residual salt levels will be periodically monitored by sampling the waste materials.

Sufficient irrigation water will be added to the cell to allow for leaching of the salts into the main collection sump. Samples of the leachate water from the individual test cells and the main leachate collection system will be analyzed on a periodic basis. Leachate volume measurements will be taken from the main leachate collection system. It is expected that the leachate waters from the early stages of the treatment will need to be deep well injected.

The test cells will be fertilized periodically based on the results of soil tests to maintain an optimum C:N ratio. Irrigation will be carried out on a frequent basis, with cultivation to follow each irrigation episode as soon as the material is dry enough to be cultivated. The quality of the leachate water will be monitored and when feasible the leachate will be recycled to the land treatment unit, to minimize fertilizer losses and reduce fresh water usage.

In an attempt to enhance the biodegradation rate, particularly for resistant heavy hydrocarbons an aeration system will be added to main leachate collection sump and a carbon source such as molasses will be added to stimulate the growth of the naturally occurring bacterial population which has developed in the test material. Once the bacteria population in the leachate sump has increased, this liquid will then be spray irrigated on the appropriate treatment cells. This increased bacterial population may increase the hydrocarbon biodegradation rate.

Laboratory Scale Studies

Laboratory scale experiments will be utilized to determine the maximum potential of certain proposed treatments. Previous land treatment trials with oily wastes did not reveal any differences in degradation rates between two rates of cultivation or fertilization (Danielson et al. 1990), perhaps due to inherent variability in the field. Controlled laboratory studies on degradation enhancement factors will provide a cost-effective means of determining the potential for using each factor being considered. For example, if bacterial inoculation were being considered to enhance oily sludge decomposition, negative results in the laboratory (based upon CO_2 evolution and substrate hydrocarbon analyses) would clearly render expensive and time-consuming Bio-Reactor field trials unnecessary. Other degradation enhancement factors that could be evaluated in laboratory scale experiments would include (1) nitrogen fertilizers: slow releases types vs fully soluble types, (2) carriers for sludges, (3) the validity of attempting to increase populations of bacteria capable of degrading hydrocarbons or recalcitrant organics by adding relatively easily degraded carbohydrates and (4) specially prepared organic residue amendments that are under development by Dearborn Environmental Consulting Services and the Wastewater Technology Centre (Burlington).

Operational Feasibility Factors

In order for this type of Bio-Reactor to be operationally feasible it must provide a reasonable cost alternative and relatively fast treatment rate. For this process to be feasible it is expected that each waste material will have to be cleaned within a single growing season. The cleaned materials will then be removed from the cell and either returned to its source of origin or disposed of as landfill cover or by landfilling. Treatment costs must be in the order of a few hundred dollars per tonne in order to be competitive with other "high tech" treatment facilities.

Once the basic Bio-Reactor design has been evaluated, if the operational costs are competitive with alternate treatment systems, it is recommended that the use of a water treatment plant be evaluated for locations where deep well injection facilities are not available.

Project Personal

Dr. Robert M. Danielson, Kananaskis Centre for Environmental Research, will act as principal investigator for this project. Representatives from each of the research groups and agencies listed in the introduction are participating in the project.

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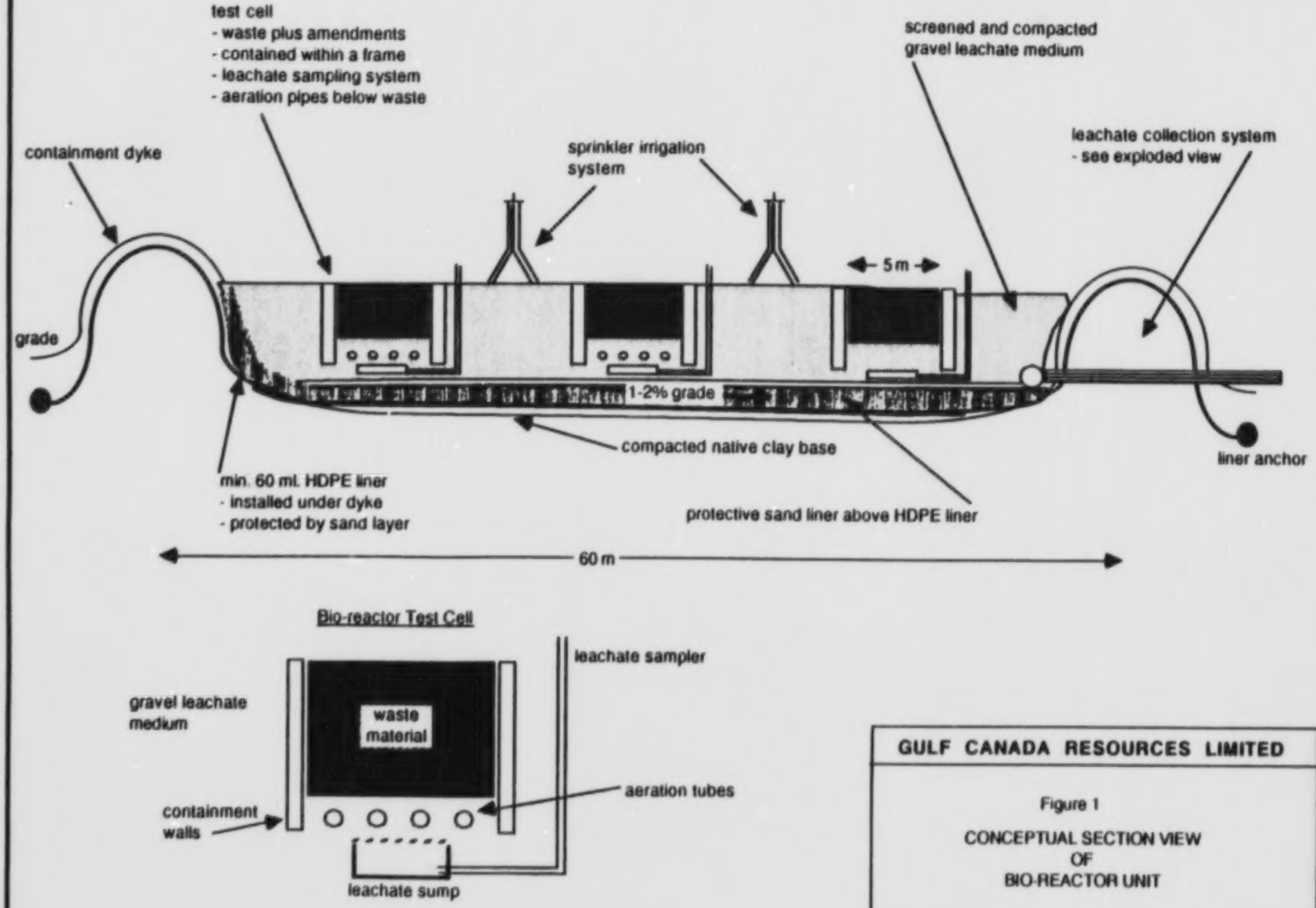
test cell
- waste plus amendments
- contained within a frame
- leachate sampling system
- aeration pipes below waste
screened and compacted
gravel leachate medium
containment dyke
sprinkler irrigation
system
leachate collection system
- see exploded view
5 m
grade
1-2% grade
compacted native clay base
liner anchor
min. 60 ml. HDPE liner
- installed under dyke
- protected by sand layer
protective sand liner above HDPE liner
60 m
Bio-reactor Test Cell
leachate sampler
gravel leachate
medium
waste
material
aeration tubes
containment
walls
leachate sump

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Figure 1

CONCEPTUAL SECTION VIEW
OF
BIO-REACTOR UNIT

Not To Scale 14/06/90

K[illegible] LAN[illegible] USE CONSU[illegible]ING [illegible]

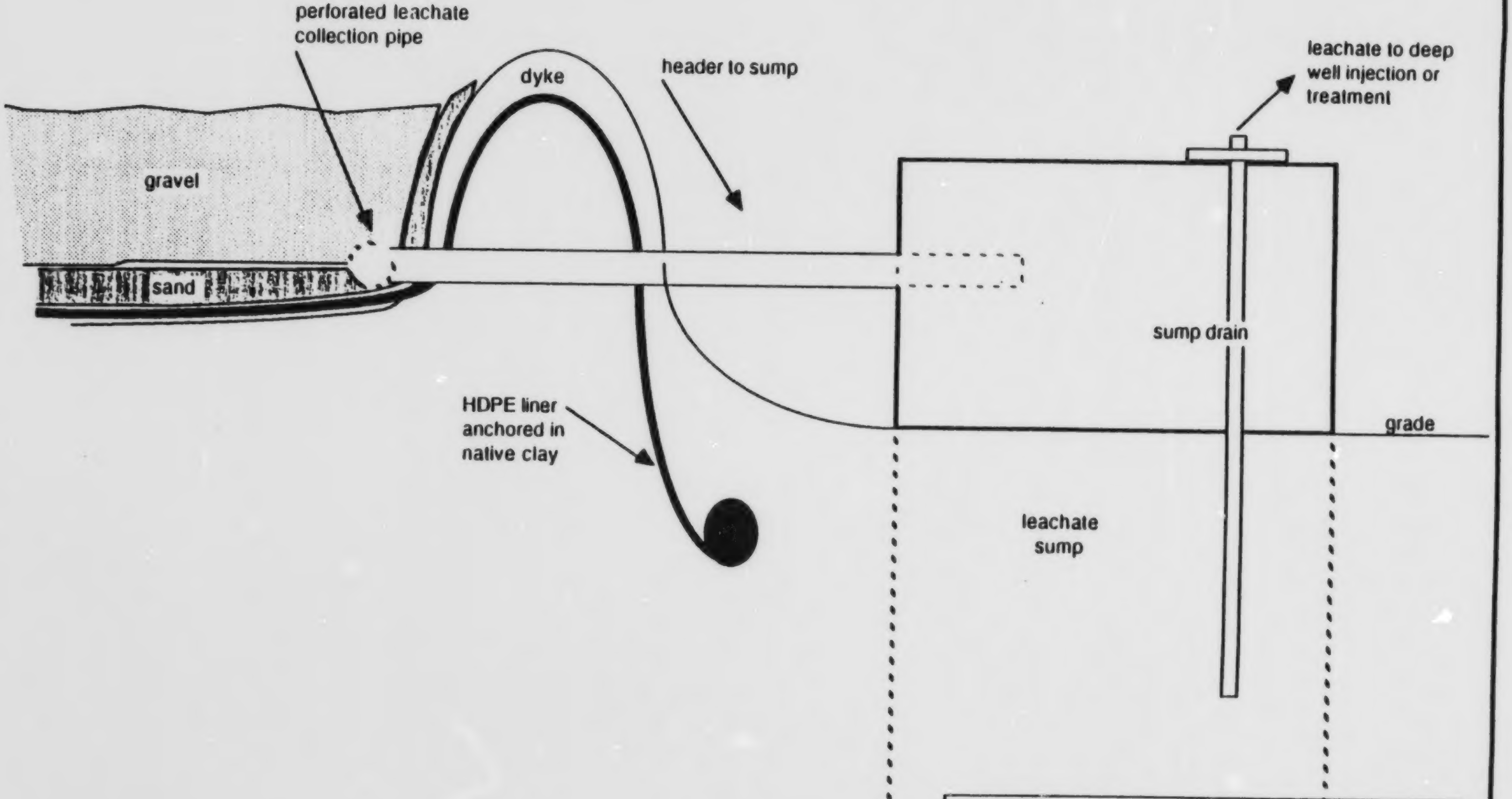
perforated leachate collection pipe
dyke
header to sump
leachate to deep well injection or treatment
gravel
sand
sump drain
HDPE liner anchored in native clay
grade
leachate sump

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Figure 2

CONCEPTUAL SECTION VIEW
OF
LINER ANCHOR AND LEACHATE
COLLECTION SYSTEM

Not To Scale

22/08/90

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IN SITU VOLATILIZATION TECHNOLOGIES
R, D & D
SCOPING STUDY

by

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As part of the National Groundwater and Soil Remediation Program (GASReP), various research, technology development programs, and field demonstration projects will be undertaken to address groundwater and soil contamination by hydrocarbons in Canada. As part of this mandate, a literature review and scoping study was initiated to examine the present state of development and use of In Situ Volatilization technologies in the unsaturated zone. The information examined in this study was restricted to hydrocarbon contaminated soil from facilities upstream and downstream in the petroleum industry. This project was conducted under the direction of the Technical Sub Committee of Soil Venting and Off Gas Treatment.

The objectives of this study were three-fold:

(i) identification of in situ volatilization technologies and documentation of current status
(ii) evaluation of the above technologies
(iii) identification of research and development requirements.

In most remedial action schemes in both Canada and the U.S.A., regulatory officials require responsible parties and cleanup contractors to use permanent and cost-effective technologies while still providing adequate protection to public health and environment. On occasions, the use of in situ technologies may provide a means of fulfilling these requirements. With a land band on solvent tainted soils in some municipalities, in situ technologies are becoming viable alternatives. They also help to control or minimize possible fugitive emissions. Such technologies may also be applied close to existing structures thereby minimizing structural instability or demolition as may be the case with excavation.

Several in situ volatilization technologies have been successfully applied to many sites with petroleum based soil contamination. However, no one technology is technically viable and cost-effective for all contamination problems. Technologies inherently are limited by the soil properties, the contaminants present, and the individual site conditions. Various technologies will be discussed.

SOIL VACUUM EXTRACTION

Soil Vacuum Extraction (SVE) is one of the most common in situ technologies used in the cleanup of contaminated soils. Other generic terms describing this technology are: forced air venting, in situ air stripping, or soil venting. Many hundreds of sites have been remediated by this means in Canada and the U.S.A.

A typical schematic of an SVE system is illustrated in Figure 1. Many of the components of the SVE system are constructed with standard process equipment. The plumbing component which includes extraction wells, injection wells, and air headers are constructed out of plastic or steel. Gas flow meters and valving are installed in strategic positions to measure or balance flow or pressure within the system. Air/water separators are used to remove excessive moisture which protects blowers and increases the vapour treatment efficiency. Optional impermeable caps may also be installed to minimize short circuiting of atmospheric air and extend the radius of influence of the vapour extraction wells within the subsurface (Hutzler et al, 1989a).

The success of the SVE process depends on the ability of the contaminant to be partitioned into the vapour phase in the soil and carried away by the SVE airstream. The soil gases are extracted mechanically by air blowers connected to air extraction wells installed in the contaminated zone(s). As the gases are extracted, a reduction in the vapour phase concentration is realized. This causes a disruption in the equilibrium concentrations between soil, liquid and the vapour phases. Due to these changes, the flux of contaminants will be directed to the vapour phase. Continued venting would further reduce the concentrations of contaminants in the soil.

Soil Properties

Favourable soil properties are required for the successful operation of an SVE process. Although SVE has been applied to sands and gravels, silts, clays, sandstone and limestone formations, it is most successful in homogeneous, free draining, high permeability soils. Any contaminants which are present on the soil, in blobs or in solution, are easily accessible by the vapour flow path induced by the SVE process in such an environment. As partitioning occurs between the liquid and vapour, or the product and vapour, the contaminant is easily removed in a continuous air-filled porosity.

Conversely, the presence of heterogeneities will cause complications for effective and complete contaminant removal. If the organic compound has percolated into finer grained heterogeneities, the removal of such compounds would be entirely dependant on a diffusion limited process. Although partitioning will occur within the fine-grained materials, the transport of the contaminant into the airstream in the higher permeability zones, is very slow. Since fine grained materials have the ability to retain pore water, the potential for vapour transport will be greatly reduced. In order for removal to occur, the contaminant would have to diffuse through the pore water and into the gaseous phase surrounding the coarser material. Although SVE will eventually result in concentration reductions, longer treatment periods may be needed to obtain a desired cleanup level.

Despite this fact, claims have been made concerning cleanup of low permeable soils and rock formations. With the use of fairly high vacuums (eg. 29.9 mmHg), some practitioners have reported remediation of contaminants from such subsurface environments (TerraVac, 1990; Burgdorf and Lambert, 1989). Although cleanup is theoretically possible, slow or non-uniform air

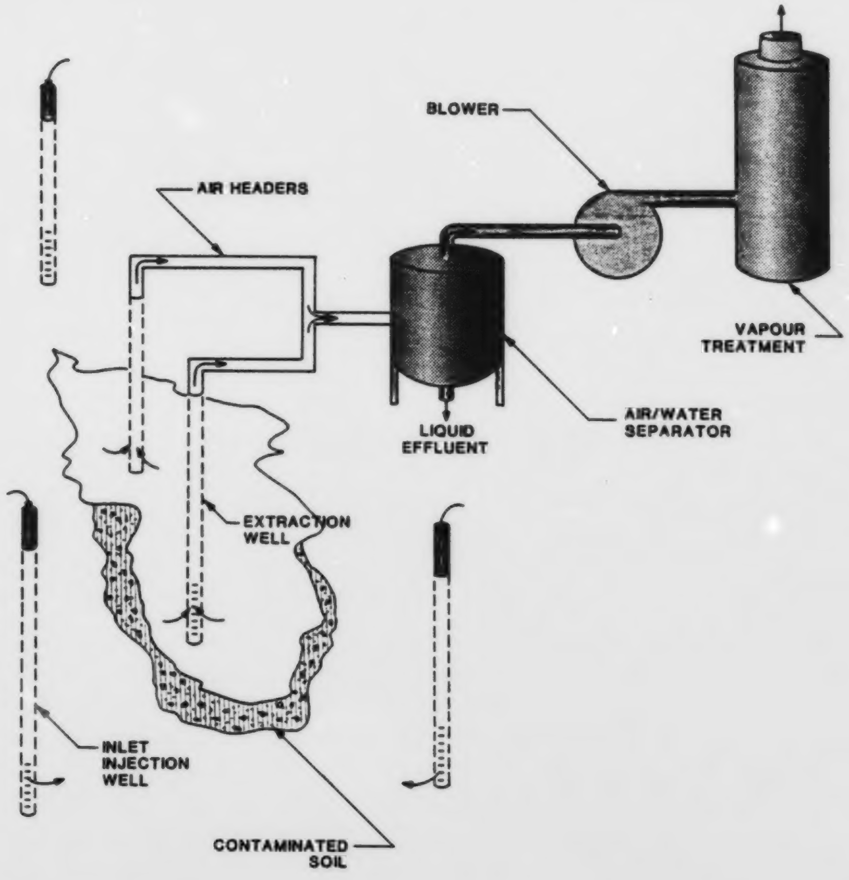

BLOWER
AIR HEADERS
VAPOUR TREATMENT
LIQUID EFFLUENT
AIR/WATER SEPARATOR
EXTRACTION WELL
INLET INJECTION WELL
CONTAMINATED SOIL

FIGURE 1: TYPICAL SCHEMATIC OF SOIL VACUUM EXTRACTION SYSTEM

flow through such soils will limit cleanup effectiveness. Providing that the volatile organic compounds (VOCs) are primarily located in the areas of high secondary permeability (i.e. fractures) removal could be rapid. If diffusion into the matrix has taken place, longer cleanup times can be expected.

The efficiency of soil gas removal is also dependent in part on the sorption affinity of a particular contaminant on the surface of the soil aggregate. A key variable effecting gaseous phase partitioning in the unsaturated zone is the degree of water vapour present. Various investigators have researched the effect of soil moisture on soils including English and Loehr (1989), Chiou and Shoup (1985), Peterson et al (1988), and Davies and Enfield (1989). Peterson et al (1988) have measured partition coefficients of trichloroethylene (TCE) with respect to soil water content in laboratory column tests. Peterson et al calculated that with a moisture content of less than 8.4 percent (which corresponded to 1.4 monolayers of water on the simulated soil material) increased sorption was noted. In a similar experiment, Davies and Enfield (1989) found that with a moisture content of 6 percent (one monolayer of water) a strong interaction between chlorobenzene (a slightly polar compound) and the mineral surface was possible. The conclusions of such research indicated that if sufficient drying of a soil were to take place, such as during soil venting (Bohn and Bohn, 1987), the removal process would be strongly retarded, even for very volatile compounds such as TCE. One field study described by Johnson and Sterrett (1988) noted that ambient air moisture correlated well with dichloropropene concentrations at a site in Benson, Arizona. However, for most studies, very little data exists for field verification of this phenomenon since most studies do not report on the degree of soil moisture conditions. At another site described by Roy F. Weston (1985), the problem of increased adsorption was not identified.

Another factor which may affect the degree of sorption (and the ultimate transport of gases) in the unsaturated zone is the amount of organic carbon content. In most cases where the soils have not been contaminated by anthropogenic carbon, the organic carbon content can be expected to be quite low. Although the upper metre of soil may have an increased carbon content, below this depth, the amount of natural organic carbon typically drops off drastically. However, in the case of an organic chemical spill, the amount of organic carbon at depth may be greatly increased. As a spill of a non-aqueous phase liquid (NAPL) (such as a petroleum hydrocarbon) occurs, a contaminated zone is left in the wake of its travel path. For most organic products, especially those of complex nature, the chemical composition is likely to change over time. Transformation processes such as volatilization, or biodegradation will cause the removal of the light fraction. Consequently, the longer chained organics are left behind. These compounds are generally less soluble, more viscous and are resistant to removal. Eventually, the residual NAPL no longer acts as a fluid and instead exists in discrete ganglia or as a thin film over the existing porous media. This residual NAPL now forms a new source of organic carbon in the subsurface (Bouchard et al, 1989a). The presence of this NAPL may have a pronounced effect on the sorption of neutral organic compounds. The effects of organic compounds have been demonstrated in the saturated zone at a spill site in Travers City, Michigan where the presence of JP4 jet fuel has caused considerable increases in sorption (Bouchard et al, 1989b). Such effects could theoretically affect SVE performance especially where a large fraction of longer chained hydrocarbons are present. The slow release of organics from the geologic material or from stationary NAPLs may also be due to slow desorption kinetics (Bouchard, 1989).

As a result of the complications of slow release discussed above, the contaminant concentrations in the exhaust stream of the SVE process follow a typical pattern. Initially concentrations are quite high and the composition comprises a large proportion of the most volatile chemicals, however, with continued venting, concentrations normally decline to some steady state value. At this stage, removal efficiencies are commonly quite low. In order to overcome this problem, some practitioners apply pulse pumping to increase removal efficiencies. The goal behind pulse pumping is to increase the removal efficient, i.e. weight of contaminant removed/energy input. Pulse pumping is only initiated when concentration in the soil gas rises sufficiently to warrant operation. In most cases, such schemes are not significantly economically advantageous.

Contaminants Removed

The chemical properties of the contaminant are the primary driving mechanisms for the partitioning process. Figure 2 illustrates three pathways for chemical partitioning into the vapour phase, two are chemical properties, the other is sorption. Providing that free product or dissolved product exists in the subsurface, it is apparent that those compounds which have sufficiently high vapour pressures and a high Henry's Law Constant are most amenable to SVE. Compounds with vapour pressures greater than 0.5 mmHg and Henry's Law Constant greater than 0.01 atm (Bennedson et al, 1987) have reportedly been successfully removed by this process. USEPA (1989) lists a set of compounds which have potential to be removed by SVE.

In cases where multi-component contamination exists in the subsurface, another factor must also be considered. The vapour pressure of the compound in the vapour phase will be affected by the mole fraction of the compound in the mixture as dictated by Raoult's Law.

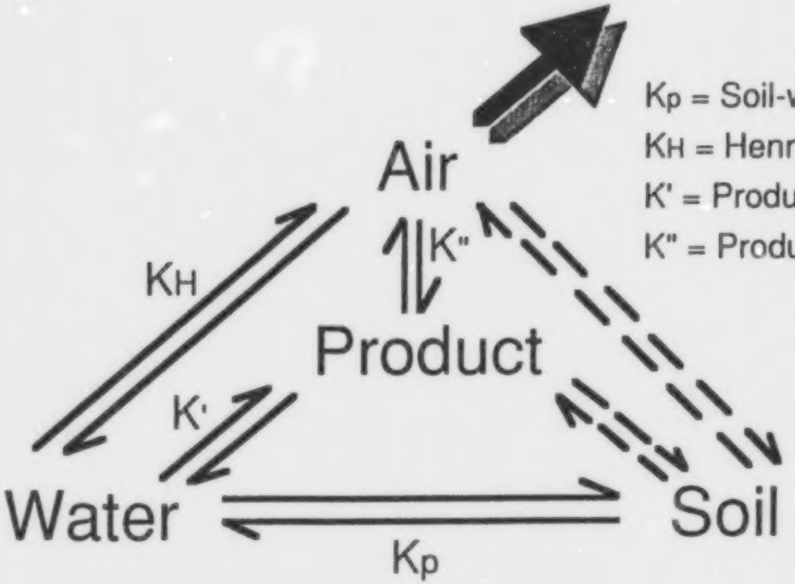
$Pa = XaPa^\circ$
where Pa = vapour pressure of solvent over solution
Xa = mole fraction of solvent in solution
Pa° = vapour pressure of pure solvent

For multi-component mixtures, such as gasoline, partitioning to the vapour phase will proceed such that lower molecular weight compounds will preferentially partition over the higher molecular weight compounds. As the SVE operation is carried out, the type of removed compound will shift towards the higher molecular weight compounds in subsequent stages of the removal process. With further removal of less volatile compounds, SVE extraction inefficiencies have been observed. (Johnson 1989)

Site Conditions

Various site conditions will also affect the performance of SVE. Hutzler et al (1989a) have indicated that the distribution of VOCs (volatile

Four Phase System


Air
Product
Water
Soil
K_H
K'
K''
K_p

K_p = Soil-water partition coefficient

K_H = Henry's Constant

K' = Product-water partition coefficient

K'' = Product-air partition coefficient

DiGiulio, 1989

FIGURE 2: PATHWAYS FOR CHEMICAL PARTITIONING IN SOIL

organic compounds), depth to the water table, infiltration rate, location of heterogeneities, temperature, and atmospheric pressure will all affect performance. Temperature and atmospheric pressure will affect the rate of partitioning and movement of contaminants in the subsurface. The infiltration rate and the location of heterogeneities will determine possible flow paths for the air stream induced by the SVE process. If the flowpaths do not occur near the contamination, performance will be affected. The depth to groundwater is also critical for the evaluation process; SVE is normally only cost-effective whenever the water table is deeper than three metres. Knowledge of the distribution of VOCs is critical for the positioning of extraction and injection wells. Without a well directed airflow, inefficient and incomplete removal may result.

One site condition which has recently received considerable attention is the case of a contaminated capillary fringe. In order to understand the impact of SVE on contaminants at the capillary fringe and on the saturated zone, a comprehension of the mechanisms at the water table is essential. The influence of SVE on product removal at the capillary fringe will largely depend on the phase separation processes of air, immiscible liquid, and water. Although pressure saturation relationships have been documented for immiscible liquids in this zone, coupling of these models to the air phase or contaminant transport has not been completed (Hoag, 1989). Some preliminary concepts of contaminant movement in the capillary fringe have been suggested by Hoag (1989).

Hoag (1989) summarized the mechanisms for two types of volatile contaminants, light and dense non-aqueous phase liquids at the capillary fringe. In the case of the light non-aqueous phase liquid, a floating product layer is often created as the contaminant reaches the water table. As infiltrating rainwater percolates through the contaminant layer, the downward movement of water will attain saturated solute conditions. If it is assumed that only downward vertical groundwater flow exists in the capillary zone, the rate of solute input into the saturated zone is limited to the infiltration capacity of the soil and the solubility of the organic compound. In most cases, this will result in the inefficient transport of contaminants to the groundwater. As such, SVE may prove to be sufficient for the efficient cleanup of contaminants without the use of pump and treat processes.

In the case of an organic compound with a density greater than water, the penetration of the contaminant into the saturated zone will be greatly enhanced. As a dense non-aqueous liquid reaches the water table, a slight depression of the water table surface is likely. As a water table fluctuation causes a rise in the phreatic surface elevation, many immiscible contaminants may become mobilized. The net result is that saturated solute conditions will exist at the top of the horizontal flow system. This will cause greatly increased contamination of the saturated zone. When the organic compounds are incorporated into the saturated zone, they will be separated from the main airstream of the SVE process by a saturated capillary fringe. Since the diffusion coefficient for most compounds is several orders of magnitude less in water than in air, the prospect of significant upward diffusion of the compounds is unlikely. In addition to this process, some of the contaminant may enter the saturated zone due to density effects. Whatever the process, SVE would likely not be sufficient to remediate the contamination problem.

At the present time, the rates of the above processes are not well understood. If the rate of incorporation of the contaminant into the saturated zone is slow, then SVE will likely have greater effects. If the rate of incorporation is quick, than the effect of SVE on the free product in the capillary zone will likely be minimal.

Cleanup Time Prediction

The complications arising from the mass transfer limitations discussed in the above sections will affect remediation time estimates. Due to the many complications which may arise, analytical approaches for cleanup times is not even attempted for most SVE applications. One attempt to arrive at a remediation time estimate was conducted at the Groveland site in Massachusetts (USEPA, 1989). The investigators at the site analyzed a series of soil concentrations along with the effluent from the blower. By establishing a target soil concentration, and using the contaminant's Henry's Law Constant and the soil-vapour partition coefficient, a gross extrapolation could be made for the desired exhaust gas concentration from the blower. Although such a method of estimating does have some merit, investigators concluded that the relationship between the extracted vapours and the soil concentrations could not be known with a reasonable degree of certainty. Complications arising from incomplete partitioning into the soil vapour phase, considerable subsurface mixing, etc. may not allow good representation of subsurface contaminant conditions (DiGiulio et al, 1990).

Other work conducted which could be helpful in regards to time estimates has been more mathematically rigorous in approach. Mathematical modelling of soil venting processes has been conducted by Hutzler et al (1989), Rainwater et al (1989b), Baehr et al (1989), and Wilson et al (1989). Some success has been achieved in bench scale or lab scale models even though the assignment of values of some parameters is difficult to ascertain. Field scale modelling has been less successful. Investigators cite uncertainties with Henry's Law Constant, the occurrence of heterogeneities within the flow domain, the uncertainty of initial concentrations and distributions, and the ambiguity of adsorption characteristics. Consequently, "screening" models such as developed by P.C. Johnson et al (1989) may be more suitable. Wilson (Personal Communication, 1989) is currently conducting modelling experiments using auto-correlation functions in order to predict cleanup times from heterogeneous geologic material. Using a range of hydraulic conductivities, a "range" cleanup times may also be evaluated. Such an approach, although not yet tested, may be more realistic in the context of real problems.

Research Needs

Research requirements and/or demonstration projects which are applicable to the topic of SVE relate mainly to mass transfer limitations inherent in the soil properties, chemical properties, and site conditions. The research requirements are tabulated below.

Soil Properties:

- What typical diffusion rates (water or air) are associated with organics trapped in fine grained geologic materials?
- Although some success has been documented for hydrocarbon removal by SVE operations in fractured rock, a lack of effective monitoring schemes exist. A detailed study in a fractured rock environment is needed.
- The role of porosity needs to be evaluated, especially as it relates to fine grained materials.
- The role of sorption/desorption has significant implications on the treatment time for SVE. The influence of moisture content and adsorption/desorption rates requires further evaluation.

Contaminants Removed:

- The role and behaviour of multi-component mixtures requires further study especially as they relate to vapour pressures, solubility, and Henry's Gas Law Constant.
- The fate of higher chained residual contamination from gasoline contamination requires evaluation.
- The documentation of improved performance of heated reinjected soil gases emerging from catalytic oxidation. Could higher boiling point compounds be volatilized?

Site Conditions:

- Heterogeneities cause operational problems for SVE. Could extraction/injection wells be placed in strategic locations to maximize the effective removal of the organic contaminants and, if so, how can well locations be determined.
- Fundamental research work is still required on the process affecting contaminant migration through the capillary fringe. Hoag (1989) has suggested some mechanisms, however this area of study still requires good fundamental research.
- Cleanup schemes in the capillary fringe require more evaluation. Schemes such as water table lowering and air injection into the water table need to be evaluated. Comprehensive test results for capillary zone remediation do not appear to be widely published.
- The prediction of cleanup times requires further work.

IN SITU AERATION

In situ aeration of groundwater has been developed based on conventional bubble aeration technology. The basic principle of in-situ aeration involves the injection of air above or below the water table for the purpose of volatilizing organic compounds. Essentially subsurface in situ aeration technology parallels the stripping of VOCs conducted commonly aboveground by means of process towers. Injection of air is accomplished through injection wells or horizontal trenches in the contaminated zone. In situ aeration is also being considered for cleanup of the vadose zone. Although limited documentation exists confirming the effectiveness of this technology, several authors claim success. Several investigators including Lowy and Thompson (1988), Umwelttechnik (USEPA, 1988), Hockman (1990), and Kaback et al (1990) have experimented with soil aeration techniques. Systems used by each of the above investigators may vary slightly in arrangement; the physical principles of air injection are similar.

Lowy and Thompson (1988) describe the implementation of an aeration trench which is installed perpendicular to the groundwater flow direction. In this system, a trench is excavated to the contaminated water layer. A horizontal diffuser pipe is installed in the bottom of the trench, and backfilled with gravel. As air is injected through the diffusers, volatile compounds within the groundwater are stripped away and collected in the vadose zone by SVE. Treatment of the soil gases is then required. This system promises to be cost-effective, according to the authors. Limitations to this system include: the need to fully intercept the vertical profile of the contaminant plume (which by this method is limited to the depth of the excavation), a sufficiently slow groundwater velocity (i.e. less than 1 m per day), and reduced accessibility for maintenance.

Umwelttechnik (USEPA, 1988) describes the use of air injection wells combined with SVE. The Umwelttechnik system uses pulsating air in the injection well. The use of pulsating air is intended to prevent channelling of subsurface air streams. Although this system has demonstrated some success, the actual radius of influence was not documented.

Hockman (Personal Communication 1990) has used in-situ aeration without the use of SVE. By assembling small diameter stainless steel piping arranged in bundles, injection wells were placed below the water table. Air was injected at a flow rate of 5 - 10 cfm. Groundwater contamination was reduced from 60 ppm to non-detect in a period of three months. It was uncertain if the use of sparing was responsible for enhancing the biodegradation or volatilizing the organic compounds which were initially present. Further testing at other sites to confirm the mechanism is scheduled. Testing for determining the radius of influence by means of measuring dissolved oxygen concentrations will also be initiated.

Another innovative method for in-situ aeration was developed by Kaback et al (1990) at the Savanna River Project. Two horizontal wells were installed adjacent to an abandoned process sewer line where contamination with perchloroethylene and trichloroethylene were identified. One well, placed at a depth of 151 to 157 feet below ground surface, was used to inject air below the water table. The length of the screen was approximately 310 feet in length. A shallower well installed at a depth of 65 to 75 feet below ground surface was installed for the purpose of SVE. The extraction process was first operated by using the shallow well. Concentrations of perchloroethylene and trichloroethylene were initially high however dropped off in a similar fashion as a typical SVE process. Monitoring wells located at distances of 25 and 50 feet from the extraction well were used to define the radius of influence. The radius of influence was based on soil gas pressures and contaminant concentrations.

The second phase of testing involved the injection of air into the lower well. This phase of testing is in its third month of operation at the time of writing (Kaback, Personal Communication, 1990). Based on the results thus far, contaminant removal has been high in the range of 11,000 lbs for the three month period. No decline in daily concentrations has been documented. When air injection was initiated, a large increase in microbial numbers was also noted. This indicates that microbial activity could be in significant factor for chemical degradation. As part of the testing program, borehole to borehole geophysical tomography has been used to evaluate the radius of influence. Seismic reflection, electromagnetic, electroimpedence techniques have been used with some success. Pulsing air instead of constant flowrate injection will be considered if microbial buildup on the well screen occurs. Future work at the Savanna River Project will also include methane injection into the lower well for the purposes enhancing anaerobic degradation.

Research Needs

Soil properties, chemical properties, and site conditions which limit the mass transfer of organic contaminants to subsurface air stream in the SVE process, are similar to the in situ aeration process. As such, research needs pertaining to mass transfer problems with the SVE, are similar in the aeration process. However, since the in situ aeration process may also be installed in the saturated zone, including the capillary fringe, additional research needs are created. Additional needs include:

- what are typical zones of influence which amy be expected from an air injection well?
- what effect has a pulsating airflow have on operating performance?
- how efficient is the mass transfer rate in the vadose zone under the influence of in situ aeration?
- what air emissions are encountered with such a process?
- modelling of biological activity under the influence of in situ aeration.

ENHANCED BIODEGRADATION

Although enhanced biological degradation is not necessarily classified as an enhanced volatilization technique, it is an important spin-off of the SVE process. Biodegradation is beyond the scope of this paper and is addressed in a parallel study commissioned by GASReP to deal solely with this topic. However, a brief discussion of the influence of soil venting on the aerobic biodegradation process will be given here.

Of the environmental factors such as moisture content, pH, availability of nutrients, etc., necessary for biodegradation, oxygen is a critical ingredient for the effective metabolization of many constituents. In the presence of oxygen, compounds such as: acetone tert-butanol, bromodichloromethane, benzene, toluene, chlorinated phenols, and naphthalene have been shown to undergo biodegradation. Whenever contaminants are located in the subsurface, water is often used as a carrier for delivering oxygen to the subsurface. The problem with this approach, however, is the low solubility of oxygen in water. Solubility limitations restrict oxygen delivery to 8 mg/L (.0008%) for dissolved air. Other methods of oxygen transport such as through the use of hydrogen peroxide can theoretically deliver 500 mg/L of oxygen (0.05%); dissolved pure oxygen can achieve a maximum dissolved concentration of 40 mg/L (.004%).

SVE offers some advantages in oxygen delivery for enhanced biodegradation when contamination is restricted to the vadose zone. By inducing a vacuum on the subsurface, oxygen transfer can be increased substantially over conventional water-based transfer techniques, Hinchee (1989). The use of SVE also offers advantages in the rate of oxygen transfer. Based on field experiments performed by Hinchee et al (1989), the breakthrough of oxygen occurs within hours of the initiation of SVE. This rate contrasts favourably when compared with weeks or even months required for transfer of oxygen via water-based transfer techniques.

An example of where SVE is applied to increase biological activity, is at Hill Air Force Base, Utah. To evaluate the effectiveness of biodegradation, carbon dioxide and oxygen were monitored before and during soil venting. Initially high CO_2 (11 percent) and low oxygen (1 percent) levels were measured. As venting was initiated, CO_2 levels declined (however, they were still a magnitude higher than atmospheric levels); oxygen levels increased. With continued venting, CO_2 levels again increased; this suggested that biodegradation was playing a significant role in the remediation process. Later, with the introduction of water, CO_2 levels again increased which indicated increased biological activity.

Soil and Site Limitations

One drawback which arises with the use of enhanced SVE biodegradation technology occurs when the organic contamination exists below the water table. Whenever the contamination is below the water table, oxygen transfer by means of continuous air flow to the area of contamination is not possible. In order to overcome this difficulty, the water table may be lowered so that the contaminated soil is exposed (Hinchee 1989). Although this technique will allow greater exposure of the airflow to the contaminated soil, appropriate disposal of the extracted groundwater may then be required.

Another drawback in the use of an SVE biological process occurs when there is a lack of nutrients and/or water in the area of subsurface contamination. In order to maximize the biological mineralization of organic compounds in the subsurface, sufficient quantities of both water and nutrients are required. Hinchee (Personal Communication, 1990) noted that significant declines in biological activity occurred whenever insufficient quantities of nutrients were not present in the subsurface. As a result, water and nutrients are introduced by means of infiltration galleries. A typical infiltration gallery is shown in Figure 3.

However the delivery of nutrients is not always efficient. Nutrients such as phosphorus can react with high mineral content water and cause precipitation. Nitrogen, which is commonly introduced as an ammonium salt, may sorb onto clays or silts due to their high cation exchange capabilities.

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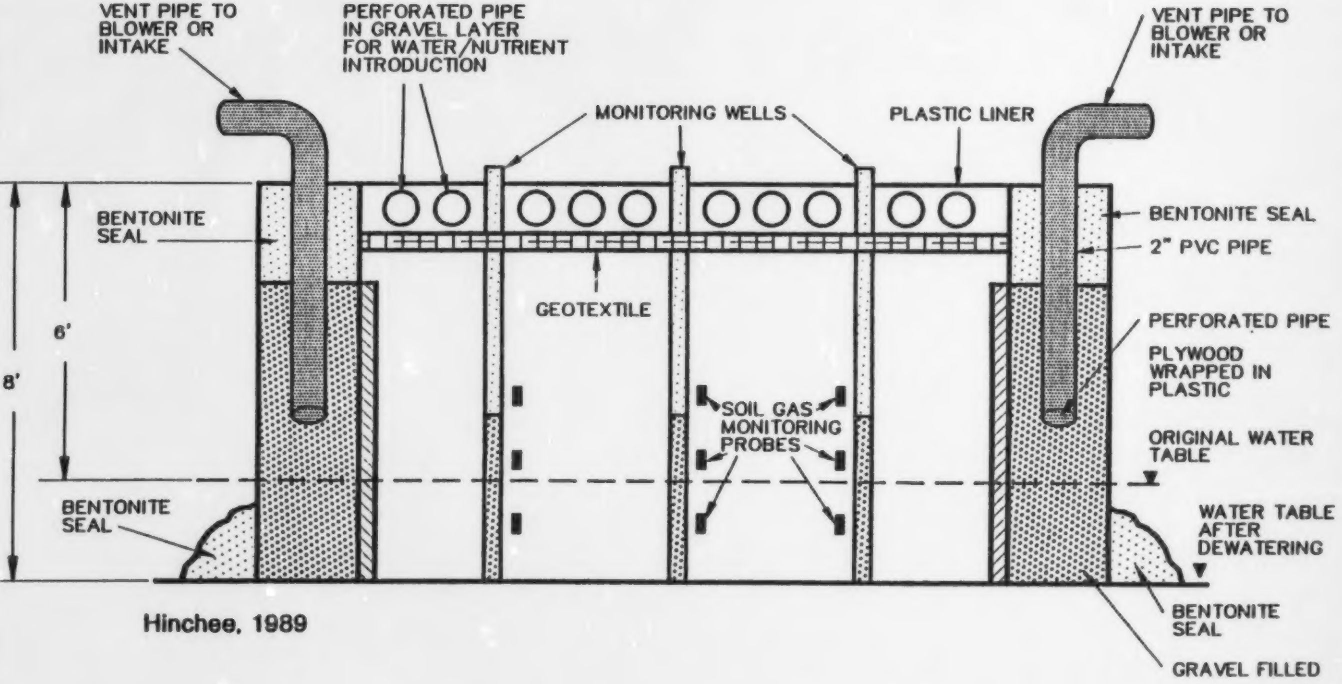
VENT PIPE TO BLOWER OR INTAKE
PERFORATED PIPE IN GRAVEL LAYER FOR WATER/NUTRIENT INTRODUCTION
MONITORING WELLS
PLASTIC LINER
VENT PIPE TO BLOWER OR INTAKE
BENTONITE SEAL
BENTONITE SEAL
2" PVC PIPE
GEOTEXTILE
6'
8'
PERFORATED PIPE
PLYWOOD WRAPPED IN PLASTIC
SOIL GAS MONITORING PROBES
ORIGINAL WATER TABLE
BENTONITE SEAL
WATER TABLE AFTER DEWATERING
BENTONITE SEAL
GRAVEL FILLED

Hinchee, 1989

FIGURE 3: SCHEMATIC FOR ENHANCED BIODEGRADATION BY SVE

CH2M HILL

Consequently, nutrient delivery is a frequent problem (R. Hinchee, Personal Communication, 1990).

The main method of monitoring of subsurface biological activity has been through the monitoring of $C0_2$ concentrations in the effluent gases. This type of monitoring however is only an indirect method of measurement. Although $C0_2$ measurements, and C^{13}/C^{12} analysis provide a qualitative assessment of subsurface biological activity, such methods are inadequate to provide an accurate measure of actual degradation of subsurface contamination. This is especially true if the airflow in the subsurface is being channelled through high conductivity zones or if only residual contamination exists. As a result, there is a need to develop alternative methods to evaluate quantitatively subsurface biological degradation activity. Other methods of analysis would be helpful to correlate with results obtained from typical $C0_2$ analysis of the effluent gases.

Research Needs

Research Needs for SVE enhanced biodegradation at this time should address:

- The delivery of nutrients to the area of contamination is a major problem. Development of better strategies is necessary.
- The development of alternative methods to assess subsurface biological activity

OZONE TREATMENT

Another technology which is not a strictly volatilization method but which may prove successful involves the use of ozone in place of air for the transformation of organic compounds. When vapour extraction systems are inefficient due to sorption effects or low volatility, as discussed previously, the use of ozone treatment may eliminate the encountered mass transfer problems (Masten, 1989). By implementing the use of ozone injection, the oxidation of organics may be achieved in-situ and thereby the removal and treatment of the subsurface gases is not required. Masten (1989) studied the use of ozone oxidation in the laboratory by simulating subsurface conditions. Contaminant compounds such as cis-DCE and PCE, as well as interferences resulting from humic acids, were studied. Although ozone did react with the aromatic portion of the humic acid, the presence of humic acid promoted the rate of ozone decomposition. Testing on simulated soils, showed that almost complete (>99 percent) decomposition of cis-DCE and approximately 40 percent decomposition of PCE was possible. Presently, it is not known whether a field test with ozone has been attempted.

Further research into ozone treatment on the lab scale is required to further understand its' potential.

RADIO FREQUENCY HEATING

Low temperature remediation technologies such as SVE have proven successful over a wide range of low boiling point compounds, however SVE has had limitations in the remediation of higher molecular weight compounds. Multi-component mixtures such as gasoline, kerosene, diesel fuel and jet fuel have a variety of both volatile and non-volatile components. Due to the lack of sufficient vapour pressures and/or low Henry's Law Gas Constants, many non-volatile compounds are not easily extracted from the soil. Processes such as in-situ radio frequency heating combined with soil venting provide a method for increasing the volatility of some of the compounds which are non-volatile at typical soil temperatures.

In-situ radio frequency (RF) heating is a technique for the uniform in-situ heating of large blocks of soil. The largest soil block treated to date was 14.27 cubic metres. Soil temperatures may be increased to the range of 150 to 400 °C with the aid of radio frequency heating. With elevated temperatures, two alternatives are available for the remediation of contaminated soils. These alternatives include: (1) thermal decontamination of soil by vaporization and recovery of contaminants, and (2) in-situ RF heat treatment in conjunction with chemical dechlorinating agents for treatment of PCB wastes (Dev et al, 1987). Only the first alternative will be discussed here.

The main components of an in-situ RF heating system are: an RF energy deposition array, an RF power generation, transmission, monitoring and control system, a vapour barrier and containment system and a gas and liquid condensate handling and treatment system. A schematic diagram of a typical RF treatment set-up is shown in Figure 4. The RF energy deposition array (the exciter array) is the main component of the RF heating process. The exciter arrays may come in two different forms. The triplate line is a system consisting of subsurface exciter arrays which are placed in three parallel rows in the contaminated soil. With the triplate line arrangement, soil temperatures in excess of 150°C are achievable. The triplate line is appropriate where soil contamination has penetrated more than one metre below ground surface. Figure 4 shows a triplate line arrangement. The alternative method of installation is the fringing-field line. In this arrangement, the electrodes are placed on the ground surface. Maximum achievable temperatures are in the range of 130°C. This second type of array is preferable for the treatment of contamination within one metre of ground surface.

The generation of heat by these different arrays is accomplished with the use of wave-bound exciters. The wave-bound exciter arrays are designed to fully contain electro-magnetic radiation within a defined volume of soil. The transmission of electromagnetic energy is not dependent on the thermal conductivity of the soil but rather the dielectric constant of the geologic material. Upon application in a field setting, the frequency is adjusted to accommodate the size of area to be treated and the dielectric properties of the material.

The remaining components of the RF heating system are entirely dependent on the energy requirements and volume of effluent gases which require treatment. The RF power source is essentially a modified radio transmitter capable of supplying the required waveform at adequate amplitude. The vapour barrier and containment system includes a cap and a vacuum source which would retrieve the soil gases. Finally the gas and liquid condensate handling system would be used to treat the effluent.

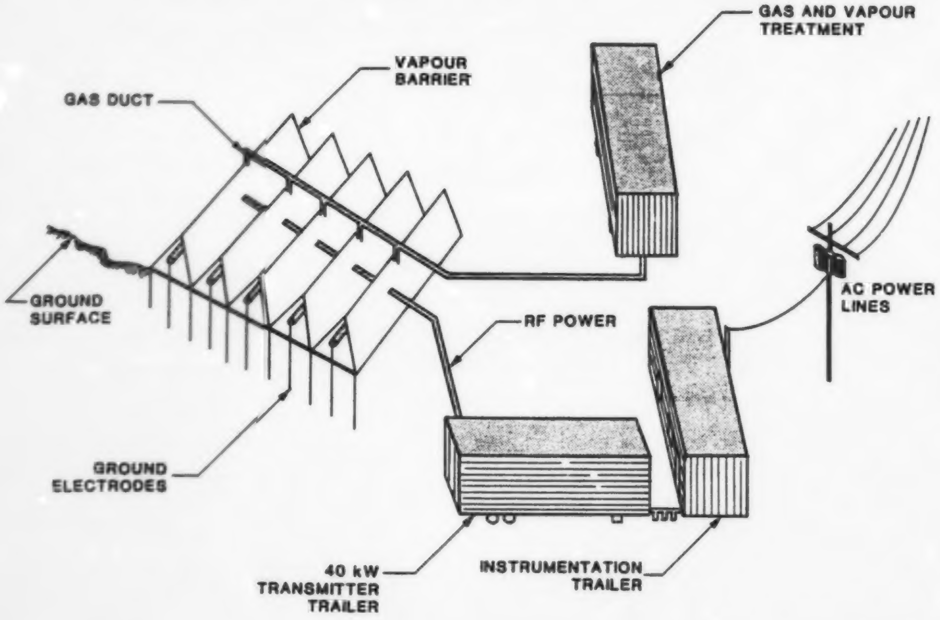
GAS AND VAPOUR TREATMENT
VAPOUR BARRIER
GAS DUCT
AC POWER LINES
GROUND SURFACE
RF POWER
GROUND ELECTRODES
40 kW TRANSMITTER TRAILER
INSTRUMENTATION TRAILER

FIGURE 4: TYPICAL SOIL TREATMENT BY RADIO FREQUENCY HEATING

Soil Properties

Although the effectiveness of RF heating has been evaluated on several types of soils in laboratory columns (Dev et al, 1988; the implementation of RF heating techniques in the field has been limited. Laboratory testing by IIT Research Institute has included testing on sandy soil and clay. Field testing has been limited to one site, Volk Air National Guard Base in Camp Douglas, Wisconsin. This site is composed of a homogeneous medium grained sand. Much of the work completed in the area of the remediation of contaminated sites has been accomplished by IIT Research Institute in conjunction with the U.S.A. Air Force Engineering Services at Tyndall Air Force Base. ITT Research Institute presently holds the patent of this technology, however, it is not currently being applied.

Plans were in place to perform a similar field study in a less homogeneous environment with more clayey soils. Laboratory results indicated that RF heating would work effectively in clayey soils. Research conducted by IIT Research Institute showed that some clays developed expanded porosity when subjected to RF heating, therefore porosity was not viewed as a problem.

Chemicals Recovered

Laboratory results on sandy soils indicate that recovery of spiked tetrachloroethylene was in the range of 94-99 percent. Heating of the soil lasted for four hours within a temperature range of 90° to 130 °C. Pilot scale studies also showed promising results. Using a 2.1 metre tall, 5 cm diameter stainless steel pipe, it was shown that 90 - 99 percent of total aromatics and total non-aromatics could be removed in 14 to 40 hours using a temperature of 150 °C to 160 °C. In the pilot test, it was also shown that compounds such as pentadecane (b.p. 270.5 °C) can be removed at 150 - 160 °C providing a steam sweep can be established in the soil (Dev. et al, 1988).

The contamination at the Camp Douglas site was due to dumped fuels and solvents over a 25 year period. Specific gas chromatography indicated an accumulation of heavy oils within the top 30 cm with an increase in lighter fuel compounds with depth. The test was run for a period of 12.5 days reaching the maximum temperature of 150 °C to 160 °C by the eighth day. Samples retrieved from the test area indicated that 89 - 90 percent of the semi-volatile aliphatics and 97 - 99 percent of the semi-volatile aromatics were removed by the ninth day. In this test, significant removal of hexadecane (b.p. 287 °C) was also observed. The removal of this compound was attributed to a steam sweep . All results were based on soil sample analysis.

Researchers are optimistic that this technology will be useful for the removal of PCBs and PAHs. Although soil studies have not been performed to acceptable remediation, preliminary cost estimates have been made and projected based on a hypothetical site. Assuming a volume of sandy soil of 2084 cubic metres, (855 sq.m by 2.4 m deep) the total cost estimate was $188,000 or approximately $70 per cubic yard of soil treated.

Research Needs

Areas of research need include:

- The use of radio frequency heating may be very important when sites have become contaminated with semi-volatile compounds. Field studies aimed at sites with PAH, and PCB contamination would be useful.
- The performance of RF heating at a clay site should be evaluated.
- The use of RF heating in deeper contamination should be evaluated. For example, contamination in a deep clay lense could be potentially remediated quickly with RF heating.
- The implementation of RF heating combined with SVE has been suggested (Downey and Elliot, 1989). Successful operation could reduce remediation times.

STEAM HEATING

The process of steam injection into a subsurface environment combined with soil venting has also been shown to have some success in the removal of both volatile and non-volatile compounds. Increasing the soil temperature by means of passing hot air or steam through the pore spaces, has the potential of increasing vapour pressures and Henry's Gas Constants. By increasing soil temperatures, a greater potential for removal of these gases will occur.

Soil Properties

Although the addition of steam into a subsurface environment has the potential to increase the volatilization of compounds, the presence of water vapour under increased pressure in a soil could potentially change the soil structure. In order to understand how steam injection could behave in a subsurface environment, laboratory experiments were performed by Lord et al (1987) at Drexel University.

In order to determine the degree of volume change which may be expected with steam injection, small laboratory columns were constructed and subjected to steam at 100°C at 1 atmosphere pressure. Tests were conducted on several different soils including loose and dense sand, silt with high and low water content, and clay with high and low water content. Of all the soils tested, all but the loosely packed sand showed volumetric increases when steam was injected. This result is beneficial for a subsurface remedial process. Whenever porosity is increased, better transport can result.

The permeabilities of several soils were also tested. By observing an advancing steam front with respect to time, investigators were able to evaluate permeabilities within the soil. The derived values were compared with standard liquid water permeabilities. Within the accuracy of the measurements, the two permeabilities were reported to be essentially the same. This indicated that the movement of a wet steam front was governed by the water permeability and not the much larger dry steam permeability. The dry steam front is defined as the high temperature front which is associated with steam injection. The dry steam front may be measured with a thermocouple.

Visual observations were also made to document the behaviour of a steam front at a stratified layer. Lord et al (1987) found that advancing steam fronts were often deflected when moving along or toward a lower permeable layer. Such behaviour could influence the remediation within a tight soil zone.

Contaminants Removed

Soil columns injected with contaminants have also been evaluated in the laboratory. The injection of steam has been performed on both unsaturated (Lord et al, 1987; Lord et al, 1989; Steward and Udell, 1989) and saturated (Hunt et al, 1988) soil columns.

Various compounds with high and low vapour pressures have been removed by steam stripping. Lord et al (1987) reported, within the limits of a somewhat crude analytical procedure, an injected gasoline was stripped from a sand column in 3 hours. In another soil of 50 percent silt/50 percent sand mixture, over 80 percent was stripped in a 3 hour period. In other preliminary work conducted by Steward and Udell (1989), analysis revealed that a reduction in total petroleum hydrocarbons of 99.95 percent was achievable with steam stripping. According to Steward and Udell, a mass transfer rate increase of 20 to 40 times is possible with steam injection compared to transfer rates at ambient conditions. In another column experiment under saturated conditions, Hunt et al (1988) injected steam into three soils each contaminated with a different compound. Contaminants included trichloroethylene (TCE), a benzene/toluene mixture, and an unleaded regular gasoline. In the first soil, nearly all the TCE was recovered after the injection of steam had taken place. With the second soil, 98 percent of the toluene, and a large percentage of the benzene was recovered. With the gasoline injected soil, no recovery estimate was available, however effluent concentrations improved from 100 mg/L (the aqueous solubility of gasoline) before steam injection, to 4.7 mg/L after steam injection. In addition to the more volatile compounds, heavier hydrocarbons have also been removed. In experiments, Lord et al (1989) report 99.9 percent removal of dodecane as well as substantial removal of polar compounds such as octanol and butanol. Based on the above examples, the potential for steam stripping is evident.

Despite the success of removal of contaminants in the laboratory, several problems have not yet been addressed. Although drier steam has been suggested by Lord et al (1987), the potential for greater adsorption may reduce the contaminant mass transfer rate. In recent experiments conducted by Lord et al (Personal Communication, 1989), kerosene was injected into a 50 percent sand/50 percent silt mixture. With only hot air as a transport medium, removal of the contaminant was not possible. Although the reason for the lack of success at this point is uncertain, potential moisture effects are possible.

Another problem identified by Lord et al (1987) is the potential for condensation. Condensation could restrict the effective removal of gases through the unsaturated zone. In laboratory columns, which were performed by Lord et al, boundary cooling effects caused condensation in portions of the soil laboratory column.

Commercial Applications

Steam injection has been implemented at field scale by several vendors in Europe and the United States. Two systems are/were being evaluated by the USEPA through the Superfund Innovative Technology Evaluation (SITE) Program. Sites which were in the SITE program were in San Pedro, California (conducted by Toxic Treatment, Inc.) and San Jose, California (conducted by Solvent Services, Inc.). At present, only Toxic Treatments is involved with the SITE program.

The "Detoxifier"™ system marketed by Toxic Treatment Inc. employs an integrated system of augers and a treatment train for detoxifying soils in-situ. The main operating component of the "Detoxifier"™ is the process tower. The process tower consists of a drill tower equipped with two hollow stem "kelly bars" mounted on top of a hollow metal shroud. The kellys are equipped with two counter-rotating turntables and auger bits mounted on the bottom of the kellys. As the kellys are turned, the augers are turned in opposite directions causing a mixing of the soil. The hollow stem kellys are also used to deliver wet/dry reagents or heated air to the subsurface. The reagents/air are expulsed through openings in the augers. Details of the system are given by Van Tassel and LaFlori (1987). A schematic of the "Detoxifier"™ methodology is shown in Figure 5.

The capability of treating heterogeneous fine grained soils which often trap contaminants is a definite main advantage of the "Detoxifier"™. The drill augers may extend to depths of 9.2 metres with the wide 1.4 metre diameter augers. As the soil is being mixed, emitted gases travel up along the outside of the kelly rods. At surface, the metal shroud is placed on the surface to collect the emitted gases. A slight vacuum draws in the gases to the process train and scrubber. As the gases have been cleaned to the specifications, they are reinjected into the kelly bars.

Based on results from soil samples before and after treatment, the "Detoxifier"™ achieved a 98.8 percent reduction of total VOCs. Apart from smaller chained hydrocarbons, the system also has shown good success in the removal of C_6 - C_{11} aliphatic/alicyclic hydrocarbons as well as C_9 - C_{10} alkylbenzenes. In general, removal of VOCs is relatively successful. The removal results of some semi-volatiles are not quite as successful, however this may be due to insufficient treatment times. Correlation with geologic material and performance data was not documented although silty soils appear to be remediated more easily than clay (La Mori and Guenther, 1989).

Costs for treating contaminated soil by means of the "Detoxifier"™ range between $100 to $300 per cubic yard of soil. Costs will vary according to location, type of treatment required, permitting, etc.

Although the "Detoxifier"™ offers advantages over other forms of treatment in heterogeneous soils, some limitations do exist. The first limitation pertains to the evaluation of treatment times. As the augers inject steam, hot air, stabilizers, etc., an adequate monitoring system to determine treatment times has not been developed. The second limitation may be due to unsuitable surface environments. If the contaminated site is adjacent to a

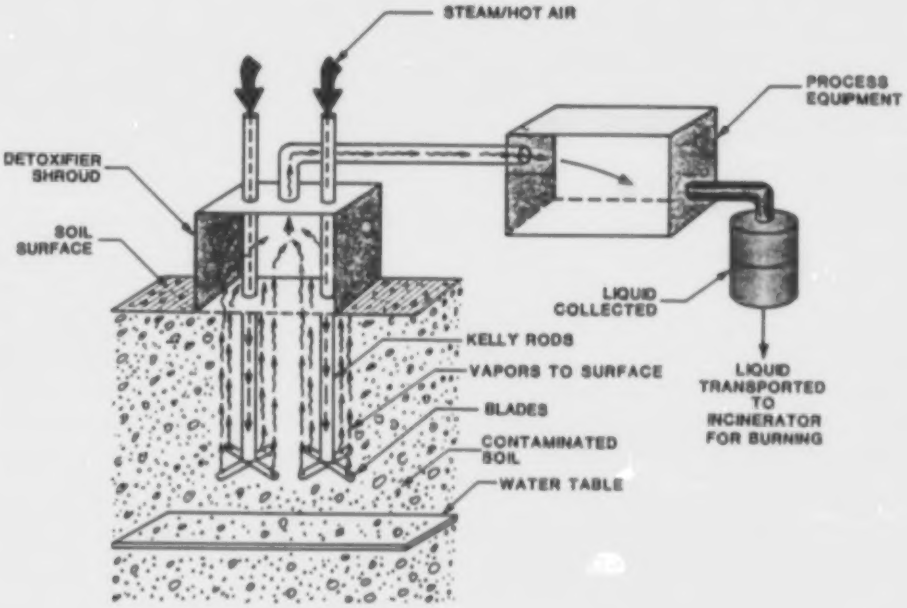
STEAM/HOT AIR
PROCESS EQUIPMENT
DETOXIFIER SHROUD
SOIL SURFACE
LIQUID COLLECTED
KELLY RODS
VAPORS TO SURFACE
BLADES
CONTAMINATED SOIL
WATER TABLE
LIQUID TRANSPORTED TO INCINERATOR FOR BURNING

FIGURE 5: TYPICAL PROCESS SCHEMATIC OF DETOXIFIER

building, in a confined space, in boulders or bedrock or close to utilities, the use of the "Detoxifier"™ may require relocation of utilities, buildings, etc.

Another method of steam injection has been implemented at Solvent Services, Inc. of San Jose, California. Details of this installation are given by Udell and Steward (1989). In order to remove contaminants from the subsurface, a steam injection system combined with SVE was implemented. A series of injection wells, a liquid sump and vapour extraction well were installed. A schematic of the set-up is shown in Figure 6. Compounds to be removed included: xylenes, ethylbenzene, 1,2-dichlorobenzene, 1,1,1-trichloroethane, trichloroethene, tetrachloroethane, and acetone. In some parts of the site, original concentrations of VOCs were greater than 1000 ppm. Some non-volatiles were also identified. Preliminary laboratory testing suggested that the site showed good potential for remediation. The rapid removal of contaminants from laboratory column work suggested that steam stripping could substantially improve the removal rates which are normally encountered with SVE.

Based on soil sample analyses, only partial success was observed in a field study. Although high permeability zones showed remarkable improvements (e.g. 1200 mg/kg to less than 22 mg/kg), lower permeability strata showed only limited removal of contaminants. The good performance of the system as seen in the higher permeability zones was mainly attributed to the use of SVE. On the other hand, the poor performance in lower permeability zones was attributed to increased mass transfer resistance between higher boiling point compounds and steam due to the initially high moisture content of these materials. The moisture content may also restrict the highly soluble compounds such as 2-butanone and dichloromethane from being transported into the gas flow.

Research is currently underway at the University of California at Berkeley to determine how much water may be vaporized by a dry steam front and whether contaminants may be removed by this process. If contaminants are removed, then steam injection has great potential at sites where heterogeneities are encountered.

Research Needs

Areas of research needed for steam extraction include:

- The role of steam extraction in the capillary fringe should be evaluated. Since steam may be effective in both a saturated and unsaturated environment, this technology may be promising for capillary fringe cleanup schemes.
- The use of steam extraction in a heterogeneous environment requires some innovative approaches. Studies on maximizing steam input into low permeability layers would be useful.
- The impact of steam condensation should be evaluated more fully. Detailed monitoring is necessary to identify problems and solutions.
- The extraction relationship of multi-component contaminants needs further study. Special attention

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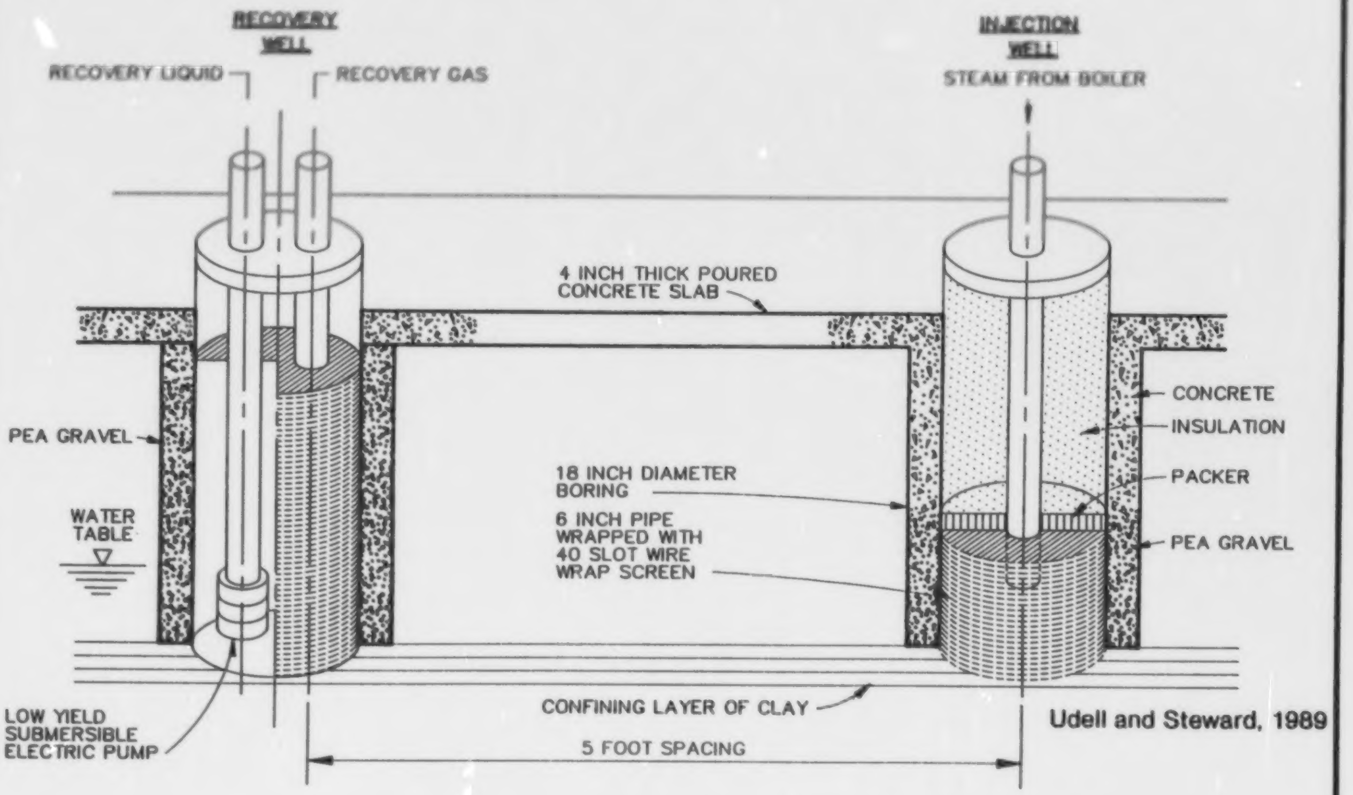
RECOVERY WELL
RECOVERY LIQUID
RECOVERY GAS
INJECTION WELL
STEAM FROM BOILER
4 INCH THICK POURED CONCRETE SLAB
CONCRETE
INSULATION
PACKER
PEA GRAVEL
PEA GRAVEL
18 INCH DIAMETER BORING
6 INCH PIPE WRAPPED WITH 40 SLOT WIRE WRAP SCREEN
WATER TABLE
CONFINING LAYER OF CLAY
LOW YIELD SUBMERSIBLE ELECTRIC PUMP
5 FOOT SPACING

Udell and Steward, 1989

FIGURE 6: SCHEMATIC OF RECOVERY AND INJECTION WELLS FOR STEAM STRIPPING

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should be aimed at investigating the extraction relationship between polar and non-polar compounds (refer to Lord et al, 1989).

CONCLUSIONS

In this study, several currently applied in situ volatilization technologies were identified and evaluated. Of the technologies identified and evaluated, no one technology is technically viable and cost-effective for all contaminated sites. Technologies are limited by soil prosperities, the contaminants present, and individual site conditions. Research, development and demonstration needs have been identified. Although limitations for some technologies may have limited possibilities for resolution, integrated approaches between various technologies have proven to be successful for overall site cleanup strategies. Various integrated approaches listed deserve due consideration as possible areas for future research, development and demonstration.

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LITERATURE REVIEW AND RESEARCH SCOPING STUDY ON THE TREATMENT OF VOLATILE ORGANIC CARBON COMPOUNDS IN THE OFF-GAS FROM CONTAMINATED GROUNDWATER AND SOIL REMEDIAL TECHNOLOGIES.

by

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INTRODUCTION

Many early attempts at site remediation, while successful at cleaning the ground-water and soil, actually increased air pollution. Emissions from contaminated groundwater air-stripping operations and from soil venting operations, which are two major sources of remedial off-gases, simply discharged the removed contaminants into the atmosphere. As recently as 1987, a survey of 177 air-stripping installations at remedial sites in the U.S. showed that only 17 had any off-gas treatment, and for most of these data were not available on the efficiencies of the processes(1).

The contaminant concentrations in off-gases from air-strippers are typically below 1000 ppmv total organics, have a high humidity, and will frequently contain chlorinated volatile organic carbons (VOCs). Soil remedial off-gases can be much more varied in concentration, and in the case of gasoline spills and leaks have been measured as high as 90,000 ppmv(2). These variations in composition of the off-gases can influence the type of treatment selected for remedial processes.

Only in the last few years have there been any attempts to destroy or contain these emissions. Consequently, very little information is available from actual remedial operations for the treatment of off-gases.

A literature survey and research scoping study was therefore undertaken, the objectives of which were:

(a) To determine the current state-of-the-art for the treatment of off-gases from remedial technologies.
(b) To determine what innovative methods were currently being researched.
(c) To determine if the processes treating industrial gaseous emissions were potentially adaptable for remedial technologies.
(d) To identify areas for future research.

Due to the lack of information from actual remedial operations the literature survey relied largely on pilot-scale work, published research, patents and industrial off-gas treatments which looked promising for application to remedial projects. This paper is a synopsis of a larger report prepared on this literature survey and research scoping study(3).

TREATMENT TECHNOLOGIES

Six off-gas treatment technologies/methods and two associated technologies were identified and are set out in Table 1. The first three are commercially available and in use at full scale cleanup operations. The last five are in various stages of development.

Each method is described in more detail below including a partial list of available units.

Table 1 : Treatment Technologies.

Commercially available.
  1. Thermal Oxidation.
  2. Catalytic Oxidation.
  3. Carbon Adsorption.

Developmental.
  4. Advanced Oxidation Processes (AOP).
  5. Biological Techniques.
  6. Membrane Separation.

Associated Technologies.
  7. Enhancement Techniques.
  8. Regeneration of Activated Carbon.

Commercially Available.

1. Thermal Oxidation.

Thermal oxidation is a rapid, simple, non-selective process and when systems are properly designed and maintained they can accomplish nearly complete destruction of VOCs. Thermal incinerators are designed to promote good mixing of air, waste gas, and auxiliary fuel (if required) prior to combustion. It is also important to have good turbulence in the combustion zone and 0.5- 1.0 second residence time. The U.S. EPA has determined that a combustion chamber temperature of 1100 °C, combined with a residence time of 1 second, can achieve at least 98% destruction of most chlorinated organics in the gas phase (1).

Thermal oxidation units are typically designed to handle hydrocarbon concentrations of 1% to 5% by volume. Lower hydrocarbon concentrations in the off-gases will increase the fuel consumption significantly. Combustion air with a heating value of less than 1.9 MJ/scm will require auxiliary fuel to maintain the desired combustion temperatures. This will frequently be the case with remedial off-gases from the air-stripping of groundwaters. For example, air-stripper off-gas with 100 ppmv benzene has a heat content of only 20KJ/scm(4). This can make the process costly for these types of remedial off-gases, which typically have high flow rates combined with a low concentration of VOCs.

There are many types and models of thermal incinerators on the market. For the treatment of off-gases from air-stripping and soil venting, it may be advantageous to use a mobile unit. Three firms offering this service are shown in Table 2.

Table 2 : Commercially Obtainable Thermal Oxidizers.(5)

Company Name	Type of Unit	Comments
Thermodynamics Corporation	Mobile Rotary Kiln	Handles all media Set-up time 2 days
NASS Inc/Supratec Inc.	Turbulator Incinerator	Handles liquids & gases, Set-up 2-3 days
Waste-Tech Services Inc.	Trailer-mounted Fluidized bed	Handles all media Set-up time 3 days

2. Catalytic Oxidation.

Catalytic oxidation is a very important industrial technique for the synthesis of partial oxidation products, such as ethylene oxide from ethylene. However there are several vital differences between these industrial processes and the complete catalytic oxidation of trace concentrations of VOCs in air.

Industrial catalytic oxidation reactions are carried out at high reactant concentrations (often 1-5 % by volume), typically at temperatures over 400°C, using a selective catalyst that is carefully chosen to promote the desired reaction (usually a partial oxidation) and to minimize any side reactions. Because oxidation is a highly exothermic reaction these processes are usually net producers of heat(6).

In contrast, the catalytic oxidation of VOCs in air-stripping emissions, is carried out at much lower reactant concentrations (typically <1000 ppmv), with a very large stoichiometric excess of oxygen. These processes are generally net users of heat, as the whole air stream requires heating to reaction temperature, and the added contribution from the heats of combustion of the organics is negligible. A highly active non-selective catalyst and the lowest possible reaction temperature (200- 500 °C) is required. The catalyst is usually a metal oxide, supported on an inert, porous media so as to give the maximum surface area(6).

In addition, the extremely high humidity of air-stripper off-gas is another factor not encountered in industry and its effect on catalyst chemistry has not been previously ascertained(7). The catalyst however may be totally or partially deactivated by chlorinated organics or other contaminants in the off-gas, thereby reducing the destruction efficiency. One method to reduce this problem is to utilize a fluidized bed catalytic incinerator, which will remove surface fouling by abrasive action. This is effective for a nonporous catalyst matrix where fouling is a surface problem. However the catalyst must be reasonably resistant to abrasion, in order to achieve a workable catalyst life of one or two years.

Only one company (ARI Technologies Inc.) claim their catalyst is resistant to poisoning by the chlorinated hydrocarbons found in remedial stripping operations. This fluidized bed catalytic oxidation process was developed jointly in the early 1970's by Air Resources Inc. and Harshaw Chemical Company. The catalyst, developed by Harshaw Chemical Company, is a nonprecious metal disposable pellet. No field data are available to support this claim, but some pilot-scale testing by Ashworth et al found that chlorinated organics destruction rates of 95-98 % could be obtained with this unit(8).

ARI and Union Carbide have recently cooperated to develop a new system employing ARI fluidized bed catalyst technology and Union Carbide molecular sieve adsorbent technology. The combined system is said to be more cost effective than catalytic destruction alone, since the catalytic unit can be scaled down by a factor of 10 or more.

Catalytic oxidation is now extensively used for the destruction of emissions of benzene, toluene, ethylbenzene, xylene (BTEX) from remedial treatment of fuel spills. In cases where the initial concentration of the gasoline vapour is in the burnable range (1.3 % by volume), a combination thermal incinerator/catalytic oxidation unit can be utilized(2).

The key to the use of catalytic oxidation for remedial off-gas treatment technologies involving chlorinated organics may be the development of non-selective and poison resistant catalysts, a subject which is currently being actively researched by several manufacturers (e.g. Johnson-Matthey).

The emissions from thermal or catalytic oxidizers may require post treatment to remove acidic gases.

Several commercial catalytic units are now on the market in North America and many others in Europe. These have been predominantly applied to the treatment of BTX in off-gases from air-stripping or soil venting. Some of the commercially available catalytic oxidation systems are shown in Table 3.

Table 3 : Commercially Available Catalytic Oxidizers(5).

Company Name	Type of Unit	Comments
ARI Technologies Inc.	Fluidized Bed Catalytic Incinerator	See above
Engelhard Corporation	Complete systems under trade name Torvex	Sizes ranging from 1700 - 120,000 m^3/hr
Groundwater Technologies Inc.	Complete systems under trade name Catalytic Scavenger	Sized for 170 - 340 m^3/hr, or 340 - 850 m^3/hr.
CE Air Preheater Combustion Engineering Inc.	Thermal and catalytic oxidation systems	Sizes ranging from 3,400 to over 170,000 m^3/hr
Johnson-Matthey Inc.	Catalyst treatment systems under trade name Honeycat	Ceramic or metal honeycomb catalyst

3. Carbon Adsorption.

Carbon adsorption has been used for many years for the removal of organics from the aqueous phase. Its use is increasing for vapour phase applications, particularly in the remedial field, and there are numerous full scale applications. Some vendors now offer mobile units for the recovery of chemical spills, with on-site regeneration of the spent activated carbon(9). There are several potential problems which must be kept in mind when designing activated carbon systems for the control of gaseous emissions.

(a) Relative humidity must be kept below 50%, otherwise the adsorptive capacity of the carbon is greatly reduced.

(b) Adsorption is an exothermic reaction, and influent hydrocarbon concentration must be kept below 40% of the Lower Explosive Limit (LEL), otherwise there is a risk of bed fires or explosion. This is rarely of importance in air-stripping of groundwater but may be worthy of consideration for soil venting of very heavily contaminated soils, especially during start up (9).

(c) The adsorptive capacity of the carbon depends on the particular hydrocarbon being adsorbed, and can vary more than an order of magnitude between different compounds. This can lead both to difficulty in sizing of the equipment and also to the displacement of one hydrocarbon already adsorbed on the carbon bed by another which has a greater adsorptive affinity. It is therefore possible for a particular VOC to appear in the effluent at a higher concentration than is present in the influent.

(d) Carbon adsorption is a non-destructive technique, and therefore will require post-treatment or disposal of the carbon. In this regard, improved methods of regeneration for the activated carbon could be the key to more economical treatment applications in the remedial off-gas field.

Some of the companies who specialize in carbon adsorption treatment units are shown in Table 4.

Table 4 : Commercially Obtainable Carbon Adsorption Units.

Company Name	Type of Unit	Comments
Calgon Carbon Corp.	Custom made to customers specification	Industrial or remedial use
Kureja, Japan	PURASIV a fluidized bed carbon adsorber	Currently industrial use only
Met-Pro Systems	KP CARBON FIBRE system, fully automated	Currently industrial use only

Developmental.

4. Advanced Oxidation Processes (AOP).

Advanced oxidation processes is a category that covers combinations of ozone and/or hydrogen peroxide and/or ultra-violet light. These treatment processes can operate at ambient temperatures and are usually less capital intensive than thermal units. However, very little actual cost and performance data are available for the AOP treatment of remedial off-gases. One of the few commercial units available a UV/ozone/catalyst process (from Ultrox International), was tested by Ashworth(8). He found that the destruction performance was poor when used without ozone, and that when ozone was used the emmissions from the unit contained three unidentified reaction products which lowered the overall destruction efficiency from 99 % to 75 %. Ultrox International has applied for a patent on the air emission control process, and are preparing to conduct further development studies under contract to the U.S Army Construction Engineering Research Laboratory. Information dissemination on these tests will be limited.(10)

A paper on the photochemical generation of ozone by Dohan & Masschelein (11), showed that ozone was simultaneously generated at 184.9nm and decomposed at 253.7nm. As the Hg-based UV emission lamps have both wavelengths present, the net production of ozone is a balance dependant on the relative proportions of the two wavelengths, which is a function of the transmittance characteristics of the lamp sleeve.

The treatment of air stripper off-gases using proprietary lamps with a much higher 184.9/253.7nm energy emission ratio than the standard low-pressure lamp has recently attracted attention from researchers(12,13). This technology, registered as Advanced Photo Oxidation (APO), has been successfully applied at two locations, one in The Netherlands and one in the U.S. No humidity control is required, as the exposure of the moist air to the UV lamps causes a simultaneous production of ozone from the oxygen in the air, free radicals from the water vapour, and photolysis and oxidation of the contaminants. In the two case studies referenced, the removal rates varied with the contaminant being treated(12).

In the Netherlands installation, a very small 3.9 cu. m/hr. unit treated 4000 cu. metres of groundwater by airstripping over a 70 day period, with an average detention time of 0.4 seconds for the off-gases in the reactor. The results were given for two tests, and these showed that the removal varied depending on the compound being treated. Removal rates were 53.5 to 66.7 % for tetrachloroethane, 77.8 to 90 % for chloroform and 94.7 to 97.5 % for trichloroethene, with an overall removal of 93.9 to 96.2 %. The method is claimed to be cost competitive with airstripping with vapour-phase carbon adsorption, ($0.27/$m^3$ for AOP versus $0.42/$m^3$ for GAC) although there is little supportive data in the literature.

The U.S. installation was described as a test site, and no details were given of capacity, flow rate, or detention time. For this test a removal rate of 99.5 % or better, was claimed for all compounds (trichloroethane, trichloroethene, tetrachloroethane).

A project, sponsored by the AWWA Research Foundation, investigated the feasibility of treating carbon tetrachloride (CTC), trichloroethylene (TCE) and tetrachloroethylene (PCE) in air stripper emissions using one or more combinations of advanced oxidation processes (AOPs) involving UV, ozone and/or hydrogen peroxide(13).

The objectives of the project were to determine the most likely candidate AOP, to optimize the operating parameters for the candidate process, and to develop cost estimates of the optimized AOP for full scale application. The processes investigated are set out in Table 5.

Table 5 : AOP Processes.

1.	UV_S	6.	UV_S/Peroxide.
2.	UV_L	7.	UV_L/Peroxide.
3.	Ozone.	8.	Ozone/Peroxide.
4.	UV_S/Ozone.	9.	UV_S/Ozone/Peroxide.
5.	UV_L/Ozone.	10.	UV_L/Ozone/Peroxide.

UV_S = shortwave UV - lamps with significant emissions below 200nm.
UV_L = longwave UV - standard low-pressure mercury lamps.

Some of the results from the study are reported in Table 6. As no AOP removed CTC the ranking of the processes was by TCE and PCE removal.

Optimization of the UV_S process involved running at four detention times (5,20,80 and 600 seconds), three UV doses (4,7 and 11 lamps), three VOC concentrations (3-4,8-9 and 10-11 ug/L in air). The results indicated that higher detention times or higher UV intensity increased the VOC removal and that the decreasing ease of removal was TCE > PCE >> CTC. The highest removal of CTC obtained was 70.9 % at 600 seconds detention time, using all 11 lamps.

Table 6 : Ranking of AOPs(13).

Rank	AOP	TCE % Range of Removals	PCE % Range of Removals
1	UV_S	87	71
2	$UV_S + H_2O_2$	79-82	64-70
3	$UV_S + O_3$	82-83	55-58
4	$UV_S + O_3 + H_2O_2$	79-82	46-57
5	$UV_L + O_3 + H_2O_2$	68-90	31-42
6	$UV_L + O_3$	80-87	28-29
7	UV_L	17	11
8	$UV_L + H_2O_2$	7-13	3-12
9	O_3	1-4	2-5
10	$O_3 + H_2O_2$	6-12	0-1

Cost estimates for the processes were based on the power requirement only for 90 % TCE and PCE removals in the air-phase AOP and compared with aqueous phase UV/ozone treatment, and air-phase GAC for the same volume of water treated. The operating costs were an order of magnitude higher than either of these processes ($0.132/$m^3$ AOP(Air), $0.008/$m^3$ AOP(Water), $0.004/$m^3$ GAC(Air)(13). The key to future advances in this field, according to these researchers, is the development of a low pressure UV lamp with substantially higher emissions in the under 200 nm range than the current low pressure lamps which emit light predominantly at the 253.7 nm wavelength.

Manufacturers are aware of this need, and are researching new formulations for lamp sleeves.

There has been very little data generated for the treatment of off-gas by this technology, and the only pilot scale unit referenced is shown in Table 7.

Table 7 : Available Units.

Company Name	Type of Unit	Comments
Ultrox International	UV/Ozone/Catalyst	Pilot scale only

5. Biological Techniques.

Only one prototype unit (the Bio-Air which is manufactured by Detox Inc.) has been used for direct biological treatment of off-gas, and this is still in the experimental stage. This fixed film unit was used to treat part of the hydrocarbon contaminated air stream from a soil venting operation. Preliminary results showed a removal of 30-80 % of the benzene, toluene, xylene (BTX) fraction(14). The contact time between the airborne contaminants and the biomass, which is a function of the air flow rate, is the limiting factor in attaining low contaminant levels in the effluent. Re-design and further testing of the Bio-Air unit is planned by Detox Inc.

The main drawbacks are the long retention times required for biological degradation and the inhibitory effects of certain chlorinated organics(11).

It is important to note that all testing to date has been performed on the off-gases from soil venting of gasoline spills, and that no off-gases containing chlorinated organics have been biodegraded in this unit. Only one prototype unit was referenced and is shown in Table 8.

Table 8 : Available Units.

Company Name	Type of Unit	Comments
Detox Inc	Fixed film unit	Experimental

6. Membrane Separation.

This is a non-destructive method used in industry for the concentration, recovery or separation of gases. Membrane vapour separation is a low pressure membrane process for separating volatile organic solvents from air. The contaminated airstream is introduced into an array of membrane modules, which each contain a semipermeable composite membrane with a large surface area packed into a small volume. Transport through the membrane is induced by maintaining the vapour pressure on the permeate side of the membrane lower than the feed airstream side. This vapour pressure difference is maintained by means of a rotary-vane vacuum pump, specially designed to treat streams containing organic solvents.

"Air and organic solvents permeate the membrane at a rate determined by their relative permeabilities and the applied vacuum. Typically, the permeate is 10-50 times more concentrated in organic solvent than the feed air. In industrial recovery processes this allows the volatile organic solvent to be easily removed by cooling and condensing the liquid".(15) The purified airstream is discharged or treated again in a second stage.

No references were found for the use of membrane separation for treating remedial off-gases. However it may well be applicable in cases where spills are recovered by soil venting operations where the concentrations of VOCs are often in the ranges of those found in industry (10,000 - 30,000 ppmv).

The main disadvantage is the requirement for multistage units in order to achieve lower emission discharge control limits. Much research work is being done in this field on the development of more efficient membranes for vapour phase applications. Therefore, application of this technology for off-gas treatment may be expected in the future.

A line of industrial vapour separation units, which claim to be best suited for airstreams containing 0.01-5 % organic solvents, and to be particularly economical for recovering hydrocarbon vapours, chlorinated and other organics is described in Table 9. The units are compact, easily transported, and all electrically powered.

Table 9 : Commercially Available Units.

Company	Type of Unit	Comments
Membrane Technology & Research, Inc.	Complete line under the name Vapor-Sep	Standard units ranging from 20-240 m^3/hr capacity

Associated Techniques.

7. Enhancement Techniques.

The off-gases produced by air stripping of contaminated groundwater typically have very low calorific values which will contribute little to the heat requirements for combustion techniques. Procedures which retain the high efficiency of these stripping units, but reduce the air to water (A:W) ratio and consequently the volume of off-gas produced, will have a profound effect on the economics of thermal post treatment processes as the requirement for supplementary fuel will be reduced. This increase in concentration and decrease in total volume of the off-gas could also improve the efficiency of biological, photo-chemical, and membrane separation techniques.

There are several off-gas enhancement techniques, these include:

(a) Using the waste heat from the thermal or catalytic oxidation to preheat the influent water. This will not only reduce the air to water ratio required, but also significantly enhance the removal of hard to strip compounds, many of which have a higher calorific value than the chlorinated organics and can reduce the heat requirements of the process. This enhancement effect is shown in Table 10.

b) Use of a more efficient air-stripping process with a lower air to water ratio than the conventional packed tower. Rotary air strippers, such as the Higee, for example give an increased VOC concentration and a smaller volume of off-gas(4). The original Higee was invented by Imperial Chemical Industries for use in the oil industry. Ashworth & Elliott (1988) reported on the performance of a unit which had been specifically manufactured for a project designed to remove jet-fuel components from groundwater(18). The Higee is a self-contained treatment system, with all components skid-mounted and ready for operation upon delivery.

The contaminated groundwater is sprayed into the centre of the rotary contactor. It is then accelerated outward through a metal packing (resembling a metal sponge) until it contacts the rotary casing and drains off. Air enters from the side and passes through the unit countercurrent to the contaminated water. The Higee was evaluated over a range of contaminant concentrations (63 - 19,000 ppb), liquid flow rates (50 - 120 gal/min), air-to-water ratios (10:1 - 170:1 vol/vol), and rotor speeds (365 - 875 rpm). Generally, removal efficiencies in excess of 99% were achieved for the fuel components studied (Benzene, Xylene). This was always true when the rotor speed was greater than 435 rpm, and the air-to-water ratio greater than 20:1. Conventional air-strippers have air-to-water ratios ranging from 30:1 to 300:1(4). Other advantages of the Higee are the ability to increase efficiency during operation, by simply increasing rotor speed, and its apparent capability to resist clogging. It is believed the high gravitational forces, and high liquid velocity in the rotary contactor increase turbulence through the packing and make the unit virtually self-cleaning. Long term runs are required to confirm this. No costing was attempted in this study, but it is anticipated that costs will be higher than for conventional air-stripping. This is because there are two power costs, one for the blower and one for the rotor drive, as against the blower only for conventional packed towers. Maintenance costs will also be higher, as it is a more complex system.

(c) The use of microporous hollow fiber membranes as the packing in a stripping column to achieve similar improvements in reducing the A:W ratio was suggested as a result of research by Semmens et al (1989)(19).

(d) The preconcentration of the off-gases on adsorbents prior to catalytic or thermal oxidation. Reference is made to the previous discussion under catalytic oxidation.

TABLE 10 : EFFECT OF HEAT ON AIR-STRIPPING PERFORMANCE(20)

Compound	% Removal at a Feed Temperature of		
	12°C	35°C	73°C
2-Propanol	10	23	70
Acetone	35	80	95
Tetrahydrofuran	50	92	>99

8. Regeneration of Activated Carbon.

Improved methods of regeneration may make the use of activated carbon a more attractive treatment alternative. For this reason the following options warrant further investigation.

a) **Biological regeneration of carbon** is being researched at the bench scale by Goeddertz(16). He has investigated the process in the aqueous phase as both a batch and a continuous process. During batch or off-line bioregeneration, an exhausted activated carbon column is removed from service and regenerated by recycling a mixture of nutrients, acclimated bacteria, and dissolved oxygen through the column. For continuous or on-line regeneration, the bacteria are grown in the column, and during times of low organic loading they obtain their nourishment by desorbing the contaminants off the carbon. The results obtained from this research may be adaptable to vapour phase installations.

b) **Carbon fibre** is a carbon adsorption system applied to the vapour phase that is sufficiently different to be discussed as a separate technique due to the fact that it is operated in a continuous adsorption/desorption cycle instead of the normal batch mode. The regenerant hot air stream contains 5 - 15 times the VOCs of the influent stream. The carbon fiber system (called KF) was developed in Japan as a superior method for recovery and re-use of solvents. It has been particularly useful for the recovery of corrosive, or reactive solvents, because of its short desorption cycle (8- 10 min). For industry its advantages over the conventional carbon beds are:

1. Higher quality of recovered solvent.
2. Less system corrosion problems.
3. Greatly reduced risk of bed fires.
4. More compact and lighter systems.

The commercial system contains two cylinders of which at any time, one is in the adsorption mode, and the other is in the desorption mode. The system is compact, can be fully automated and may be skid mounted for mobility(10). Although there are no references to its use in the remedial field these mobile units may become of importance when combined with soil venting techniques, for emergency response to spills of fuel or other volatile organic chemicals.

c) **Catalytic regeneration of carbon** successfully investigated in 1974 by Nwankwo and Turk, is an intriguing possibility. So far it has been investigated only on a very small laboratory scale, but may well justify further research(17). The investigators impregnated GAC with a platinum catalyst, and after saturating the GAC with various organics they passed a stream of air through the heated carbon. The organics were oxidized well below the ignition point of the carbon, which could then be re-used for further adsorption. In one test this cycle was repeated ten times with no loss in weight of the carbon, and only about 15 % loss in its adsorptive capacity.

SUMMARY OF CURRENT AND FUTURE RESEARCH AND DEVELOPMENT.

Some areas in which improvements may be anticipated from current research now being undertaken by manufacturers have been identified above. These include, improved low pressure UV lamps, poison resistant catalysts for catalytic oxidation, and improved efficiency for membrane separations.

The ozone/UV/catalyst system is also being investigated by Ultrox, and biological fixed film technology by Detox.

Of the processes discussed in this paper, only thermal oxidation may be considered a fully developed technique. It has been widely used for destruction of BTX in off-gases from remedial operations. Although hard data on destruction efficiency have not been available, its widespread use in the United States implies that State and/or Federal criteria are being attained.

Catalytic oxidation has been proven in the industrial field, but has been little documented for remedial work, in particular for chlorinated organics. Questions remain concerning efficiency and catalyst life.

Carbon adsorption installations when properly designed and maintained can efficiently remove organic constituents from the off-gas. However as it is a containment not a destruction process, it requires post-treatment or disposal. Research into improved methods of regeneration of the activated carbon is required.

Advanced oxidation processes and biological techniques are in the very early development stage for remedial use.

No reference to the remedial use of membrane separation has been found, however for spills involving large quantities of gasoline, recovery of the gasoline by membrane separation may be a viable treatment possibility that could be explored.

Off-gas enhancement techniques show promise for the reduction of operating costs in most off-gas treatment technologies.

Development of a data base incorporating cost information is required in order to evaluate the various technologies.

These needs are summarized in Table 11.

Much work remains to be done before the damage to our soil and groundwater can be halted and reversed, and the efficient containment and destruction of the off-gases resulting from remedial treatment techniques is an important segment of this task.

Table 11 : Summary.

Technology	Current Status or Needs
Thermal Oxidation	Fully developed technology
Catalytic Oxidation	Requires development of a non-selective poison resistant catalyst
Carbon Adsorption	Requirement for further research on methods of regeneration and the Carbon Fibre Technique
Advanced Oxidation Processes	UV Lamps with enhanced emmissions below 200 nm. Data on UV exposure times for destruction of different VOCs
Off-Gas Enhancement Techniques	Scale up of high temperature air stripping Long term testing of rotary air strippers Testing of packings and column design
Biological Regeneration	Requires scale up of current work and investigation of vapour phase application
Catalytic Regeneration	Only small bench scale experimental work has been carried out on this technique
Carbon Fibres	Commercially available but not yet tried in remedial field
Other	Development of a national data base

ACKNOWLEDGEMENTS.

Thanks are due to Bruce Jank, Jim Schmidt, and Alex Lye for their assistance in reviewing this paper.

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TELEPHONE CONVERSATIONS.

(T1) Evan K. Nyer, Past president of Detox Inc. Dayton, Ohio. 45459
USA. (513)433-7394.
Subject: Bio-Air reactor.

IRON AND MANGANESE REMOVAL FROM GROUNDWATER: ENHANCED AERATION PROCESS

by

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INTRODUCTION

Roughly forty percent of the public water supplies in the United States have iron and manganese above their respective recommended maximum concentrations of 0.30 mg/L and 0.05 mg/L(1). Although the presence of iron and manganese is generally associated with groundwater, these metals are also found in surface water.

The problems associated with the presence of these two metals in any waters extend beyond factors of aesthetics and potability. In addition to physical fouling problems, iron and manganese may stimulate biological growth, e.g. Pseudomonas/Iron Bacteria, in groundwater wells, in groundwater treatment plants, in distribution systems and in reservoirs.

The contamination of groundwaters by undesirable organic compounds has resulted in the development of treatment trains aimed at the removal of the organics of concern. However, when ferrous and/or manganous ions are present in the groundwater, treatment efforts have to focus initially on the removal of these inorganics prone to precipitation. This will minimize physical and biological fouling of the downstream unit processes responsible for the removal of the organics of concern.

The present study, which is the focus of this paper, will investigate effective iron and manganese removal trains in order to overcome the physical and biological fouling problems caused by the presence of these elements in groundwater.

BACKGROUND

During 1988-89, a bench-scale and pilot-scale R, D&D site remediation project was conducted in Ville Mercier, Québec, under the auspices of Environment Canada's Wastewater Technology Centre. One of the objectives of the project was the demonstration of an effective iron removal train, as a pre-treatment prior to the removal of the organic contaminants found in that groundwater(2). In order to fulfil this objective, several iron removal trains were evaluated at pilot-scale for their ability to remove iron effectively. These are presented in Table 1. In addition, attempts were made to minimize capital and operating costs for the train, and also sludge production. The concentration ranges for some of the key parameters found in that groundwater are presented in Table 2.

The study resulted in the selection and subsequent optimization of a simple iron removal train consisting of a diffused aeration tank followed by rapid, direct sand filtration. The performance of this train was evaluated in a continuous mode of operation during the period of May-August 1989. The total iron content in the effluent stream from the sand filter was consistently below the 0.30 mg/L objective. Design and operating parameters for the train are tabulated in Table 3. It should be noted that these parameters are specific to the Ville Mercier groundwater, and should be developed through experimental work for groundwaters with different geochemistry.

During the study, the catalytic effect of ferric iron to promote ferrous iron oxidation in the sand filter column was observed. Figure 1 illustrates these findings. The remaining ferrous iron found in the effluent stream of the aeration column was consistently removed from the groundwater during sand filtration. The mean rate of conversion of ferrous iron to ferric iron, i.e. ferric formation, was 82% in the aeration column, and 100% in the sand filter. The postulated mechanism

TABLE 1 IRON REMOVAL TRAINS (Ville Mercier, Québec)
1. Chemical Oxidation - Coagulation - Flocculation - Sedimentation - Sand Filtration
2. Chemical Oxidation - Sand Filtration
3. Diffused Aeration - Coagulation - Flocculation - Sedimentation - Sand Filtration
4. Diffused Aeration - Chemical Oxidation - Sand Filtration
5. Diffused Aeration - Sand Filtration

Reference: 2

TABLE 2 KEY PARAMETERS IN THE GROUNDWATER OF VILLE MERCIER, QUÉBEC

PARAMETERS	VALUE		
	Minimum	Maximum	Mean
Iron (mg/L)	3.00	10.80	8.78
Manganese (mg/L)	0.33	0.50	0.42
Alkalinity (mg $CaCO_3$/L)	276	317	297
Hardness (mg $CaCO_3$/L)	707	857	790
pH	6.50	7.40	6.90
T (°C)	8	12	9

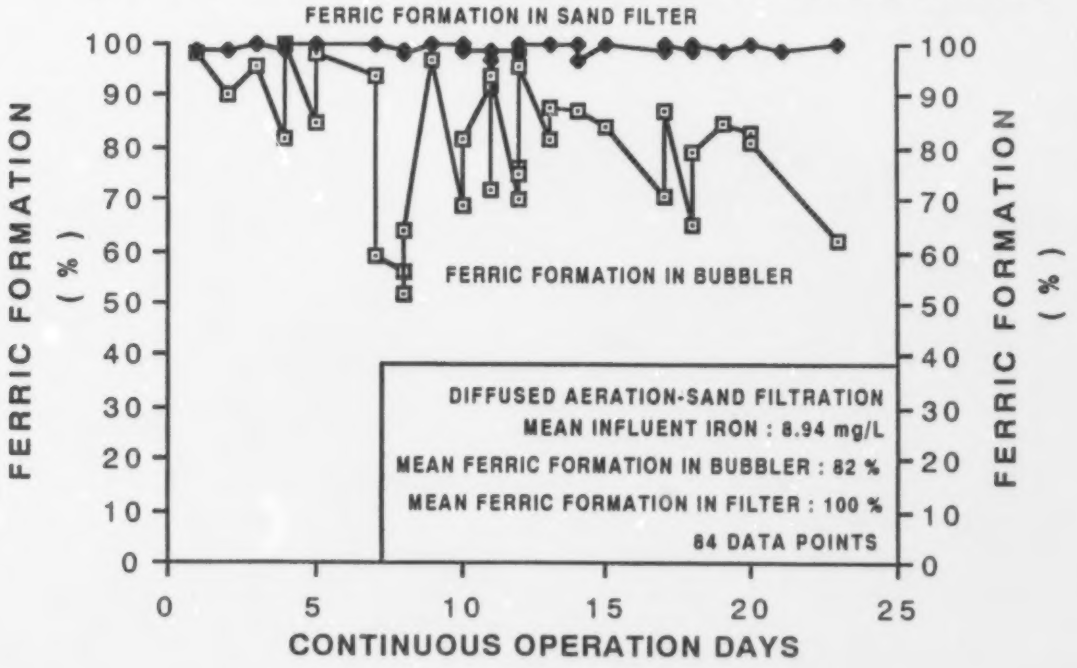
Reference: 2

TABLE 3 DESIGN AND OPERATING PARAMETERS FOR THE DIFFUSED AERATION-SAND FILTRATION TRAIN (Ville Mercier, Québec)

DIFFUSED AERATION:	FINE BUBBLE DIFFUSION HYDRAULIC RETENTION TIME: 22 min AIR TO WATER RATIO: 5.5:1
GRANULAR MEDIA FILTRATION:	SAND BED DEPTH: 110 cm SAND NOM DIAMETER: 0.46 mm SAND UNIFORMITY COEFF: 1.44 GRAVEL BED DEPTH: 30 cm GRAVEL SIZES: 20 cm/1.3 cm FILTRATION VELOCITY: 19 m/h

Reference: 2

FIGURE 1: CATALYTIC OXIDATION OF FERROUS IRON IN SAND FILTER



consists of 1) adsorption of ferrous iron onto ferric coatings on the sand filter media, and 2) subsequent oxidation of the adsorbed ferrous iron to ferric iron.

Sarikaya (1990) reported similar findings of oxygenation of ferrous iron catalyzed by ferric hydroxide(3). In addition, Sarikaya stated that ferrous iron oxygenation and iron removal improved, following the build-up of ferric iron precipitates on contact aerators, multiple-tray aerators and granular filter media in several water treatment plants.

The Ville Mercier study also demonstrated a biofouling control technology, developed by F.J. Dart (Ontario Ministry of the Environment), to abate and control the growth of Pseudomonas in the sand filter. The addition of zinc granules to the sand filter's bed was shown to be a simple and highly effective means of controlling the growth of Pseudomonas. This technology will be evaluated in the present study.

STUDY PURPOSE

The purpose of the present investigation will be to study the catalytic effect of ferric hydroxide on the oxygenation of ferrous and manganous ions in two groundwaters - one from Ville Mercier, one from the Region of Waterloo. Design and operational requirements for the proposed recycle treatment train, referred to as the Enhanced Aeration Process, will be evaluated against the diffused aeration process.

STUDY OBJECTIVE AND AIM

The objective of the present study is to increase the kinetics of oxidation for ferrous and manganous ions in an aeration column. This will be achieved by recycling a stream rich in ferric hydroxide to the aeration column to promote adsorption/catalytic oxidation of the ferrous and manganous ions present in the raw groundwater.

The aim of the present study is to minimize:

1) the size of the aeration tank, i.e. minimize the hydraulic retention time of the groundwater in the aerator,
2) the air requirement to effect the oxygenation reactions,
3) capital and operating cost for the suggested iron removal train, and
4) sludge production.

STUDY STRATEGY

The present study was subdivided into eight (8) tasks. These are presented in Table 4, together with the status for each task.

EXPERIMENTAL PROGRAM

In order to evaluate the Enhanced Aeration Process, experiments will be conducted at laboratory-scale and pilot-scale.

McGill University will conduct laboratory jar tests to compare the kinetics of iron and manganese oxidation following the addition of various amounts of ferric hydroxide in an aerated reaction vessel.

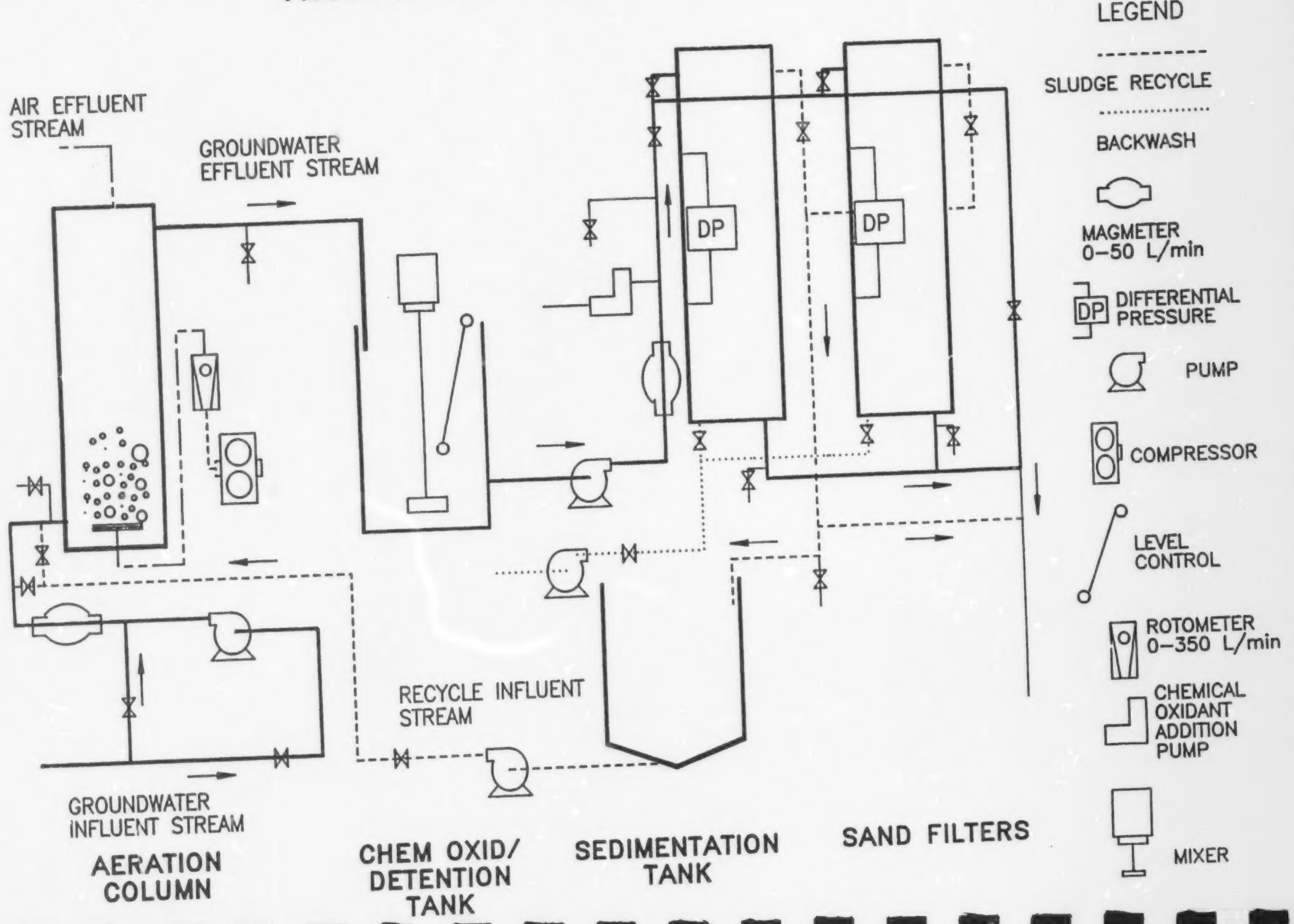
A customized, fully equipped trailer with pilot-scale equipment and analytical facilities is being built by the Wastewater Technology Centre, and is near completion. The trailer incorporates an aeration bubble column, two sand filter columns, a clarifier and a chemical oxidation tank/detention tank. The schematic of the pilot plant is presented in Figure 2.

Experiments will focus on the use of a ferric hydroxide-rich stream directed to the aeration column. Two options will be evaluated: first, a fraction of the effluent stream from the aeration column will be recycled back to the influent line of that column; and second, the sludge collected from the backwash of the sand filter, will be added to the influent line of the aeration column. The outcome of the two investigations will be to identify the concentration of ferric hydroxide required to effectively promote the adsorption/oxidation of ferrous and manganous ions.

TABLE 4 STUDY STRATEGY

#	TASK	STATUS
1.	Elaborate a work plan.	Completed.
2.	Review of the available literature on iron and manganese removal.	Near completion.
3.	Identify the groundwater sources to be used in the study. Assess types and levels of inorganic (and organic) constituents.	Two (2) groundwater sources were identified (refer to text). Inorganic and organic scans were completed.
4.	Select a list of specific inorganic (and organic) compounds to monitor throughout the study.	Completed.
5.	Develop analytical procedures to conduct all possible analytical determinations on-site. Elaborate a QA/QC programme.	Near completion. An analytical "wet chemistry" method is being developed for the determination of manganous/manganic ions.
6.	Design, construct and install a bench-scale and/or pilot-scale treatment train.	Near completion.
7.	Conduct experimental program.	Experimentation will be initiated once Tasks 1 to 6 are completed.
8.	Prepare the final report.	

FIGURE 2 : PILOT PLANT SCHEMATIC FLOW DIAGRAM


AIR EFFLUENT STREAM
GROUNDWATER EFFLUENT STREAM
DP
DP
RECYCLE INFLUENT STREAM
GROUNDWATER INFLUENT STREAM
AERATION COLUMN
CHEM OXID/ DETENTION TANK
SEDIMENTATION TANK
SAND FILTERS
LEGEND
SLUDGE RECYCLE
BACKWASH
MAGMETER 0–50 L/min
DP
DIFFERENTIAL PRESSURE
PUMP
COMPRESSOR
LEVEL CONTROL
ROTOMETER 0–350 L/min
CHEMICAL OXIDANT ADDITION PUMP
MIXER

Provisions were also made to include, in the pilot-scale setup, chemical oxidant addition points between the aeration column and the sand filter column. If required, the supplementary requirement for oxidant(s) addition will be investigated in order to carry the oxidation of manganese to completion. Furthermore, the addition of zinc granules to one of the two sand filter beds will be evaluated to control the growth of microorganisms, i.e. Pseudomonas.(3) The evaluation of this technology will be conducted while running the recommended iron removal train for 21 days or more. A condensed version of the experimental work plan is presented in Table 5.

TABLE 5 EXPERIMENTAL WORK PLAN

Action Number	Parameter	Range
1. *Conventional Aeration Process*	Q_{GW} Q_A/Q_{GW}	Design Nominal Flow 2.50 to 15.00
2. *Enhanced Aeration Process (I): Aerator effluent recycled to influent line*	Volumetric Recycle Ratio $\left(\frac{\text{aerator effluent}}{\text{aerator influent}}\right)$ $Q_A/Q_{GW\ \text{optimum}}$	0.10 to 0.20 0.25 to 1.00
3. *Enhanced Aeration Process (II): Ferric iron sludge addition in Aerator*	Iron Concentration Increase (in aerator)	1.00 x to 5.00 x
4. *Chemical Oxidant Addition (to supplement Mn Oxidation, if required)*	H_2O_2, $KMnO_4$, ClO_2	0.25 x stoichiometric requirement to 2.00 x stoichiometric requirement
5. *Performance Evaluation of the Suggested Train in a Continuous Mode of Operation*	Time	≥ twenty-one (21) days
6. *Final Report Write-up*		

STUDY LOCATIONS

The following two sites were selected for experimentation:

1. Waterloo, Ontario. With the assistance of the Regional Municipality of Waterloo, the Wastewater Technology Centre will conduct the evaluation of the Enhanced Aeration Process.
2. Ville Mercier, Québec. With the assistance of the Québec Ministry of the Environment, McGill University will conduct a preliminary evaluation of the Enhanced Aeration Process.

SUMMARY

To date, two studies have been initiated to demonstrate the Enhanced Aeration Process.

The pilot-scale experimental work, in conjunction with the Regional Municipality of Waterloo, is scheduled to commence in February 1991. The estimated date of completion is May 1991. The projected total cost of the study, including the construction of the customized pilot trailer, is $176,000.

The laboratory-scale experimental work, in conjunction with McGill University/MENVIQ, was initiated in September 1990 and is scheduled to be completed in May 1991. The projected total cost of the study is $5,000.

This research will lead to the development of a simple, yet effective process for the pretreatment of iron and manganese and control of biological growth which will be a benefit to pump-and-treat remediation systems.

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SITE SELECTION FOR DEMONSTRATION AND EVALUATION OF TECHNOLOGIES FOR REMEDIATION OF GASOLINE SPILLS

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A site has been selected as the first phase of the National Groundwater and Soil Remediation Program (GASReP) objective to demonstrate and evaluate developing technologies for remediation of gasoline spills. Subsequent phases of this research will involve detailed characterization of this site and application of various available technologies to clean up the site.

The careful selection of a suitable site for completion of these demonstrations is imperative to ensure that the results clearly reflect the performance of the technology being demonstrated and not uncertainties due to characteristics of the test aquifer. To simplify the interpretations and aid in the evaluation of the remedial technologies the main requirement of a suitable test site is a simple, uniform geology and hydrogeological flow system contaminated by dissolved gasoline. The hydrogeological characteristics of the ideal test site would be analogous to the shallow sandy aquifer at the Borden experimental site which is perhaps the worlds most highly characterized aquifer. A shallow groundwater condition is desired to reduce costs of equipment and installations for monitoring the demonstrations. A sufficiently large site will permit operation and comparison of several methods in isolated cells.

The factors which are considered most important for a suitable site are:

1) the presence of a dissolved BTEX plume,

2) the existence of a groundwater flow system which is suitable for detailed studies,

3) the size of the dissolved BTEX plume, and

4) the feasibility of completing the research at the site.

A weighted rating system modelled after the USEPA DRASTIC system (Aller et al., 1985) was developed to evaluate potential research sites. DRASTIC is used to assess the groundwater pollution potential of an area by subjecting the hydrogeologic setting to a relative ranking which considers the major hydrogeologic factors which affect groundwater vulnerability. The system developed here replaces the hydrogeologic factors of DRASTIC with factors which reflect the relative suitability of the site attributes for the proposed research demonstrations. Each attribute was assigned a weighting which reflects its relative importance in determining the site suitability. The site attributes considered in the evaluation and their assigned weightings are listed on Table 1.

The site attributes which were considered to be most important are depth to water table, material homogeneity, groundwater velocity, and presence of suitable contamination. Other attributes considered in the evaluation include, type and amount of information available, location, and logistic considerations. In some instances additional information was obtained as necessary to assist in the evaluations.

TABLE 1. SITE ATTRIBUTES AND WEIGHTING FACTORS CONSIDERED IN WEIGHTED RATING SYSTEM.

	WEIGHT
BACKGROUND INFORMATION AVAILABLE	
Hydrogeological Assessment	1
Borehole Logs	2
Groundwater Chemistry	2
Hydraulic Monitoring	1
HYDROGEOLOGICAL SETTING	
Water Table Depth	10
Saturated Aquifer Thickness	6
Aquifer Materials	7
Material Homogeneity	8
Hydraulic Conductivity	3
Hydraulic Gradient	2
Groundwater Velocity	10
CONTAMINANT DISTRIBUTION	
Nature of Contamination	10
Impacted Aquifer Dimension:	
Length	6
Width	6
Source Type	1
SITE CHARACTERISTICS	
Location	1
Site Access	3
Installation Consideration	1

To perform the site evaluations each site attribute listed in Table 1 is numerically rated between 0 and 5 according to site suitability criteria for that attribute as summarized on Table 2. To complete the evaluation for each site the product of the rating and weighting for each attribute are summed to produce a numerical ranking. The maximum score possible is 400. When applied to a group of potential sites the relative rankings reflect the suitability for use as a resarch site.

Although the numerical ranking is useful, it remained possible for a sites with one undesirable quality, for example, a bedrock aquifer, to achive scores comparable with sites which were suitble but less than ideal in most attributes. To circumvent this difficulty a simple logical decision program was included in the evaluation system which would identify the presence of undesirable qualities. Figure 1 is a flowchart which summarizes this decision process. If an attribute was truly undesirable, then the site was recommended to be eliminated from further consideration. If an attribute was possibly undesirable, the program would recommend obtaining additional information and repeating the evaluation. If the attributes were desirable the program would recommend retaining this site for consideration.

TABLE 2. SITE SUITABILITY CRITERIA FOR RATING INDIVIDUAL ATTRIBUTES.

RATING	ATTRIBUTE: CRITERIA
	Hydrogeological Assessment: REPORT QUALITY
5	- complete, highly detailed, minimal additional testing required.
3	- partially complete,some additional testing required.
1	- preliminary, additional testing necessary.
0	- no report available.
	Borehole Logs & Material Descriptions: COVERAGE/QUALITY
5	- excellent coverage, distribution, detailed descriptions.
4	- good coverage, distribution, detailed descriptions.
3	- partial coverage, some additional holes required.
1	- minimal coverage, additional holes necessary.
0	- no boreholes completed.
	Groundwater Chemistry Data: DATA QUALITY
5	- complete, fully characterized, minimal additional testing necessary.
3	- partially complete,some additional testing required.
1	- preliminary, additional testing necessary.
0	- no data available.
	Hydraulic Monitoring Data: DATA QUALITY
5	- complete, long term monitored, flow system well characterized, minimal additional monitoring required.
3	- partially complete,some additional monitoring required.
1	- preliminary, additional monitoring necessary.
0	- no data available.
	Water Table Depth: DEPTH RANGE
5	0 - 1 m
4	1 - 3 m
3	3 - 5 m
2	5 - 7 m
1	7 - 10 m
0	> 10 m
	Saturated Aquifer Thickness: SATURATED THICKNESS RANGE
5	> 5 m
4	2 - 5 m
1	1 - 2 m
0	< 1 m

TABLE 2. SITE SUITABILITY CRITERIA FOR RATING INDIVIDUAL ATTRIBUTES (continued).

RATING	ATTRIBUTE: CRITERIA
	Aquifer Materials: RELATIVE GRAIN SIZES
5	- sands, gravelly sands.
3	- silty sands, sandy till.
1	- silt, till.
0	- clay, rock.
	Material Homogeneity: HOMOGENEITY
5	- uniform, single component system, ideal.
4	- relatively uniform, easily predictable.
3	- mixed system, some inhomogeneities, predictable.
2	- inhomogeneous, not easily predictable.
1	- inhomogeneous, complex bedding relationships, not predictable.
0	- very inhomogeneous; fractured rock, undesirable.
	Hydraulic Conductivity: HYDRAULIC CONDUCTIVITY
5	10^{-4} m/sec
4	10^{-3} or 10^{-5} m/sec
3	$10^{-5} - 10^{-6}$ or $10^{-2} - 10^{-3}$ m/sec
0	$< 10^{-6}$ or $> 10^{-2}$ m/sec
	Hydraulic Gradient: HYDRAULIC GRADIENT
5	- low, horizontal, uniform
4	- moderate, horizontal
3	- high horizontal
2	- minor vertical component
0	- dominant vertical gradient
	Groundwater Velocity: GROUNDWATER VELOCITY
5	5.0 - 15.0 cm/day
4	1.0 - 5.0 cm/day
3	15.0 - 25.0 cm/day
2	0.5 - 1.0 cm/day
1	5.0 - 50.0 cm/day
0	< 0.5 or > 50.0 cm/day
	Nature of Contamination: NATURE OF CONTAMINATION
5	- petroleum product + dissolved phases, BTEX presence confirmed.
4	- dissolved phase identified, BTEX presence confirmed.
3	- petroleum product + dissolved phases, BTEX presence not determined.
2	- dissolved phase identified, BTEX presence not determined.
1	- contamination not characterized.
0	- no dissolved BTEX, confirmed.

TABLE 2. SITE SUITABILITY CRITERIA FOR RATING INDIVIDUAL ATTRIBUTES (continued).

RATING	ATTRIBUTE: CRITERIA
	Impacted Aquifer Dimensions: LENGTH
5	> 30 m
4	20 - 30 m
3	10 - 20 m
1	< 10 m
0	Dimensions not known.
	Impacted Aquifer Dimensions: WIDTH
5	> 60 m
4	40 - 60 m
3	20 - 40 m
2	10 - 20 m
1	< 10 m
0	Dimensions not known.
	Source Type: SOURCE TYPE
5	- long term continuous release, unremediated
4	- continuous release, large spill, partially remediated.
3	- occasional release, moderate size spill, partially remediated.
2	- small spill, unremediated.
1	- spill, partially remediated.
	Location: DISTANCE FROM WATERLOO
5	< 50 km
4	50 - 100 km
3	100 - 150 km
2	150 - 200 km
1	> 200 km
	Site Access: ACCESSIBILITY
5	- very good, minimal interference from current on-site activities.
4	- good, some interferences.
1	- poor, some interferences.
0	- very poor, major complications, interferences.
	Installation Considerations: INSTALLATION EASE
5	- shallow system, very easy, manual methods, existing techniques.
4	- moderately shallow, manual methods not preferred, existing techniques.
3	- moderately deep, drill rig preferred.
1	- deep system, drill rig required.
0	- very difficult, new techniques required.

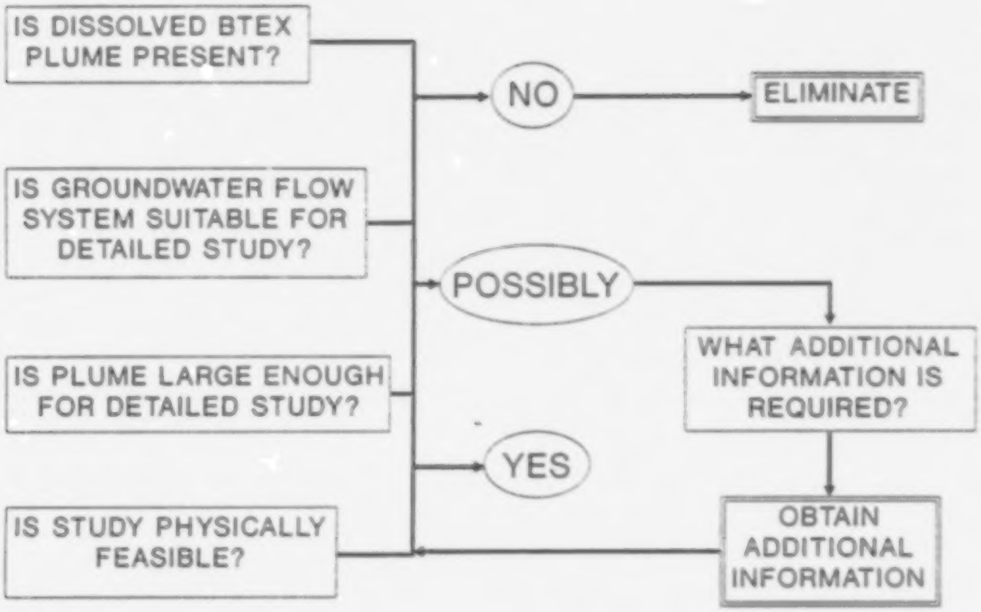
IS DISSOLVED BTEX PLUME PRESENT?
IS GROUNDWATER FLOW SYSTEM SUITABLE FOR DETAILED STUDY?
IS PLUME LARGE ENOUGH FOR DETAILED STUDY?
IS STUDY PHYSICALLY FEASIBLE?
NO
ELIMINATE
POSSIBLY
WHAT ADDITIONAL INFORMATION IS REQUIRED?
YES
OBTAIN ADDITIONAL INFORMATION

FIGURE 1. DECISION FLOWCHART FOR SITE EVALUATION.

To demonstrate the application of this evaluation system two fictitious sites were created, one with attributes which were suitable for use as a research site and one which was unsuitable. These attributes are summarized on Tables 3 and 4 respectively. The results of the suitability evaluation for these fictitional sites is summarized on Tables 5 and 6. The rating system successfully identified the better site with a higher numerical ranking and a lack of undesirable qualities, and recommended further consideration. If a real potential site had received a similar rating preliminary investigations would have been undertaken to confirm the presence of a dissolved BTEX plume and the ranking would have been repeated.

The site selection process involved obtaining information describing 14 potential sites with histories of gasoline contamination. The site information was provided by Esso Petroleum Canada, Petro-Canada, Sunoco Canada, Department of National Defence, the Prince Edward Department of the Environment, and their engineering consultants. Sites considered were located in various parts of Ontario, Prince Edward Island, and Labrador. In the interests of client confidentiality the sites have been assigned a reference letter for the following discussions. The numerical ratings and recommendations for the 14 sites are listed on Table 7.

Site C has been chosen as the preferred site for hosting the *in situ* remedial demonstrations. Site C placed lower than sites A and B in the ranking due to a relatively deep water table, however other attributes are highly favourable for hosting the proposed research. Site A is not preferred due to a lack of dissolved BTEX in the contaminant plume and the remote location. Site B is suitable, however the geology is somewhat complex and there are difficulties obtaining access and permission.

At Site C gasoline spills have occurred over a discrete surface area at regular intervals for more than 30 years. Investigations completed as part of this site selection process have identified a large plume of dissolved gasoline moving away from the source at approximately 20 cm/day. The site is underlain by more than 15 m of uniform glaciolacustrine sand and the water table depth varies between 7 and 14 m. Activities to fully characterize the site and identify appropriate remedial technologies to be demonstrated are underway.

TABLE 3. CHARACTERISTICS OF A FICTITIOUS SITE SUITABLE FOR RESEARCH STUDIES.

BACKGROUND INFORMATION AVAILABLE	**SITE CHARACTERISTICS**
Hydrogeological Assessment	Partially complete
Borehole Logs	Additional boreholes required
Groundwater Chemistry	Additional sampling required
Hydraulic Monitoring	Additional monitoring required
HYDROGEOLOGICAL SETTING	
Water Table Depth	5-7 m
Saturated Aquifer Thickness	2-5 m
Aquifer Materials	Silt, silty sand
Material Homogeneity	Mixed system, predictable
Hydraulic Conductivity	10-5 m/sec
Hydraulic Gradient	High gradient, horizontal
Groundwater Velocity	20 cm/day
CONTAMINANT DISTRIBUTION	
Nature of Contamination	Dissolved BTEX not confirmed
Impacted Aquifer Dimension:	
Length	25 m
Width	50 m
Source Type	Occasional release
SITE CHARACTERISTICS	
Location	Oshawa
Site Access	Industrial, some interferences
Installation Consideration	Drill rig may be required

TABLE 4. CHARACTERISTICS OF A FICTITIOUS SITE UNSUITABLE FOR RESEARCH STUDIES.

	SITE CHARACTERISTICS
BACKGROUND INFORMATION AVAILABLE	
Hydrogeological Assessment	Minimal, insufficient
Borehole Logs	Preliminary only
Groundwater Chemistry	Preliminary only
Hydraulic Monitoring	Preliminary only
HYDROGEOLOGICAL SETTING	
Water Table Depth	8 m
Saturated Aquifer Thickness	1.5 m
Aquifer Materials	Fractured rock
Material Homogeneity	Heterogeneous, complex
Hydraulic Conductivity	10-1 m/sec
Hydraulic Gradient	Vertical
Groundwater Velocity	50 cm/day
CONTAMINANT DISTRIBUTION	
Nature of Contamination	Not determined
Impacted Aquifer Dimension:	
Length	5 m
Width	10 m
Source Type	Small spill
SITE CHARACTERISTICS	
Location	Ottawa
Site Access	Major site difficulties
Installation Consideration	Drill rig required

TABLE 5. EVALUATION OF A FICTITIOUS SITE SUITABLE FOR RESEARCH STUDIES.

	WEIGHT	RATE	SCORE
BACKGROUND INFORMATION AVAILABLE			
Hydrogeological Assessment	1	3	3
Borehole Logs	2	3	6
Groundwater Chemistry	2	3	6
Hydraulic Monitoring	1	3	3
HYDROGEOLOGICAL SETTING			
Water Table Depth	10	2	20
Saturated Aquifer Thickness	6	4	24
Aquifer Materials	7	3	21
Material Homogeneity	8	3	24
Hydraulic Conductivity	3	3	3
Hydraulic Gradient	2	3	6
Groundwater Velocity	10	3.5	35
CONTAMINANT DISTRIBUTION			
Nature of Contamination	10	3	30
Impacted Aquifer Dimension:			
Length	6	4	24
Width	6	4	24
Source Type	1	3	3
SITE CHARACTERISTICS			
Location	1	3	3
Site Access	3	4	12
Installation Consideration	1	3	3
TOTAL SCORE		57.5	256

DECISION:

CONFIRM BTEX
AQUIFER MATERIALS SATISFACTORY - PURSUE
HYDROGEOLOGY SATISFACTORY - PURSUE
IMPACTED DIMENSIONS SATISFACTORY - PURSUE
SITE ACCESS SATISFACTORY - PURSUE

TABLE 6. EVALUATION OF A FICTITIOUS SITE UNSUITABLE FOR RESEARCH STUDIES.

	WEIGHT	RATE	SCORE
BACKGROUND INFORMATION AVAILABLE			
Hydrogeological Assessment	1	1	1
Borehole Logs	2	1	2
Groundwater Chemistry	2	1	2
Hydraulic Monitoring	1	1	1
HYDROGEOLOGICAL SETTING			
Water Table Depth	10	1	10
Saturated Aquifer Thickness	6	1	6
Aquifer Materials	7	1	7
Material Homogeneity	8	0	0
Hydraulic Conductivity	3	0	0
Hydraulic Gradient	2	0	0
Groundwater Velocity	10	0	0
CONTAMINANT DISTRIBUTION			
Nature of Contamination	10	1	10
Impacted Aquifer Dimension:			
Length	6	1	6
Width	6	1	6
Source Type	1	2	2
SITE CHARACTERISTICS			
Location	1	1	1
Site Access	3	1	3
Installation Consideration	1	1	1
TOTAL SCORE	80	15	58

DECISION:

CONFIRM BTEX
UNDESIRABLE MATERIALS - ELIMINATE
VELOCITY UNSUITABLE - ELIMINATE
IMPACTED DIMENSION TOO SMALL - ELIMINATE
SITE ACCESS DIFFICULTIES - ASSESS

TABLE 7. SUMMARY OF SITE EVALUATIONS.

SITE	RATING	EVALUATION
SITE A	335	Potentially suitable: confirm BTEX presence
SITE B	326	Potentially suitable: investigate access
SITE C	315	Suitable: Confirm possibility of access
SITE D	306	Potentially suitable: investigate access
SITE E	304	Potentially suitable: assess
SITE F	303	Potentially suitable: investigate access
SITE G	225	Unsuitable: No BTEX Present
SITE H	218	Potentially suitable: extreme access difficulties, plume not defined
SITE I	209	Unsuitable: Sandstone Aquifer
SITE J	205	Potentially suitable: confirm BTEX, size, access
SITE K	201	Potentially suitable: confirm BTEX, size, access
SITE L	194	Unsuitable: Poor hydrogeology
SITE M	185	Unsuitable: No BTEX Present
SITE N	183	Unsuitable: Bedrock Aquifer

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REMEDIATING SUBSURFACE CONTAMINATION AROUND SOUR GAS PROCESSING FACILITIES: OPPORTUNITIES FOR FIELD RESEARCH, DEVELOPMENT AND DEMONSTRATION

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ABSTRACT

A multi-phase study of subsurface contamination at Alberta sour gas processing facilities has been initiated by the Canadian Petroleum Association and Environment Canada. Phase I, completed in 1989, identified the most frequently occurring groundwater and soil contamination situations at Alberta gas plants, based on a review of monitoring data from 54 plants provided by Alberta Environment. The study found that of the 45 plants for which information allowed assessment of the presence of groundwater contamination, only one showed no signs of impact of plant activities on groundwater. The findings of the phase I study have highlighted the need for some consideration of subsurface remediation technologies appropriate to the unique combinations of potential contaminants, hydrogeology and climatic conditions found at sour gas plants in Alberta. Phase II of the project was initiated in November of 1989, and is presently underway. This phase of work involves identification, prioritization and selection of subsurface remediation technologies applicable to the particular contamination situations identified in Phase I. New and innovative technologies worthy of field- or bench-scale testing will also be identified. A concurrent effort is underway to contact operators of seven gas plants identified as suitable sites for technology demonstration projects, and solicit formal support and participation from them. Starting in the middle of 1991, selected technologies will be matched with participating plants, and opportunities for field demonstration of remediation various systems finalized. The Canadian Petroleum Association and Environment Canada will be seeking the participation of groups interested in conducting research-oriented field trials of selected technologies.

1. INTRODUCTION

Background

Much of the natural gas produced in the province of Alberta contains hydrogen sulphide gas, or H2S. Concentrations of H2S in produced gas can vary from a few part per million to over 90%, depending on the source. Natural gas containing hydrogen sulphide is commonly called "sour gas". Processing of sour gas involves the removal of the H2S from the gas stream, and its conversion to elemental sulphur through a variety of techniques. Sales of sulphur are an important source of revenue to plant operators. Other by-products of the processing include natural gas liquids (condensate), produced water, CO2, and process wastes. There are at present over 150 sour gas processing plants operating in Alberta (Oilweek, 1987).

Sour gas processing plants produce a wide variety of products and wastes which have the potential to impact the subsurface, including process chemicals such as amines, glycol and sulphinol used to remove H2S from the gas stream, sulphur and sulphur products, hydrocarbon liquids and their dissolved components (such as BTEX), and highly saline produced waters. These substances can be delivered to the subsurface in many forms by a number of mechanisms, and all have the potential to seriously degrade soil and water quality.

Rationale and Objectives

Recognizing the potential impacts of sour gas plant operations on the subsurface environment, the Canadian Petroleum Association and Environment Canada have launched a multi-phase study focusing on demonstrating remedial technologies for soil and groundwater contamination at these facilities. The first phase was initiated in 1989, and consisted of a comprehensive review of all soil and groundwater monitoring data submitted to Alberta Environment by sour gas plants in accordance with the Clean Water Act (1971). The review indicated that all but one of 45 sour gas plants reviewed exhibited some form of impact on soil and groundwater quality (Piteau Engineering Ltd, 1990; Hardisty et al, 1990). The study identified the most frequently occurring contamination situations at 45 plants, and classified them according to sources and types of contaminants, and the hydrogeological characteristics of the geologic host. The findings and specific recommendations of this phase of the study are discussed in section 2.

The results of the first phase of the study provided the first step in an investigation of subsurface remedial technologies applicable to the unique environmental, hydrogeological, climatic, and economic conditions found at Alberta sour gas plants. The new climate of public concern and regulatory commitment to the environment has spurred developments of numerous technologies for clean-up of contaminated soil and groundwater. Some have been available for several years, and are widely used in the USA and parts of Europe and Canada, while others are relatively new and have not undergone rigorous field trials.

The purpose of the second phase of this study, now underway, is to select the remedial technologies most appropriate for the most common contamination situations at Alberta sour gas plants, and thereby provide a framework for implementation of one or more pilot subsurface remediation demonstration projects. A parallel goal is to identify new and innovative technologies which show promise for application at these sites and are worthy of further field or bench-scale testing.

In tandem with this study of appropriate remedial technologies, another consultant is presently engaged in the task of soliciting formal support for the implementation of field demonstration projects in the near future. Phase I of the study identified seven sour gas plants in Alberta whose subsurface contamination situations and level of site characterization were suitable for field demonstration purposes. The operators of these seven plants are being approached; two or three will be selected for the demonstration phase of the project, based on their willingness to participate in all aspects of the project.

The technology study and operator selection phases will be completed simultaneously. At that time, selected technologies will be matched with appropriate sites, and demonstration projects selected and designed. One of the most important goals of the overall project is to provide opportunities for research into subsurface remediation systems suitable for sour gas plants and other petroleum industry installations.

2. SUBSURFACE CONTAMINATION AT ALBERTA SOUR GAS PLANTS

Data and Methodology

The first phase of the study was based on groundwater monitoring data provided by Alberta Environment, and consisted of documents submitted to the Standards and Approvals Division by plant operators pursuant to the Alberta Clean Water Act. In all, information was obtained for 54 Class B sulphur-recovering sour gas plants. The quality and completeness of information contained in the reports were quite variable. Soil sampling data were not available in the Alberta Environment records. Data from six of the 54 plants were obtained directly from plant operators. Of the 54 plants considered, sufficient data for adequate appraisal of subsurface contamination situations were available for 32. Information from 13 of the remaining plants allowed partial contamination assessment only.

The variability in data reporting reflects to a large extent the lack of standard groundwater monitoring and data reporting guidelines for sour gas plants in Alberta. Alberta Environment is presently working on a new set of guidelines for groundwater monitoring at industrial and waste disposal facilities in the province, although at this time it is uncertain when these will be available.

The available data for each gas plant were reviewed and where possible groundwater contamination situations identified. Contamination situations were classified based on the source and types of contaminants, and the physical properties of the geologic host. No assessment of the seriousness (or the perceived need for clean-up) of the various contamination situations was undertaken, as in the majority of cases insufficient data were available for this task. Current guidelines do not specify provision of evaluations of the fate of contaminants by operators.

Groundwater Contamination

Of the 45 plants for which information allowed assessment of the presence of groundwater contamination, only one showed no signs of impact of plant activities on groundwater quality. Since the initial review, indications of groundwater contamination have also been found at the one plant which was originally classified as having no contamination.

There were sufficient data available at 42 plants to determine sources of groundwater contamination. Table 1 shows the number of plants with at least one contamination situation originating from each of the source categories. Thirty-three of the 42 plants (78.5%) had at least one contamination situation originating from the process water/evaporation pond. Other common sources of groundwater contamination were process areas and on-site landfills. The sulphur block area was also identified as a frequent source of contamination. Other sources of contamination which were identified included surface runoff drainage ditches and ponds, injection wells on-site, and product loading areas.

There were sufficient data available at 44 plants to determine the types of contaminants in groundwater. Dissolved inorganic and organic species were the most commonly identified groundwater contaminants; these include chloride and sulphate ions, aromatic hydrocarbons, amines and other process chemicals. Impact on groundwater quality by sulphur products, notably sulphate and in some cases acid seepage waters, were identified at 17 of the 45 plants. Of interest, however, is that wherever monitoring wells were installed downgradient of sulphur blocks and storage areas, contamination was detected (only 17 of the plants surveyed had extended their monitoring systems to include sulphur facilities).

Free phase condensate contamination was identified at five plants. Although this number represents only about one-tenth of the plants surveyed, the relative concern attached to this type of contamination makes it of particular interest. Free phase hydrocarbon contamination is difficult and expensive to remediate, and very low levels of hydrocarbon render water unfit for human or animal consumption. Table 2 shows the number of plants with at least one contamination situation involving each of the six major contaminant groups.

TABLE 1
NUMBER OF CONTAMINATION SITUATIONS DETERMINED AT GAS PLANTS
(Total of 45 Surveyed)

Number of Situations per Plant	Number of Plants	Cumulative Number of Plants
4 or more	10	10
3	12	22
2	14	36
1	8	44
none	1	45

TABLE 2
TYPES OF GROUNDWATER CONTAMINANTS
Number of Plants where the
Indicated Contaminant type
was Identified at Least Once
(Total of 44 Surveyed)

Type	Number of Plants	Percentage of Plants
Main Ions	42	93.3
Dissolved Organics	41	91.9
Sulphur Products	17	37.8
Free Hydrocarbon	5	11.1
Metals	3	6.7

It must be noted that findings were affected by the analytical schedules which the various operators chose to apply to their groundwater samples. If more comprehensive analysis of groundwater quality had been done, additional contaminant types may have been identified. Data with which the location of groundwater contamination could be determined were scarcest in the reports provided by Alberta Environment for this study. In many instances, borehole logs or piezometer construction details were not available, making it very difficult to determine which groundwater-bearing zone was being sampled. As a result, the nature and hydraulic properties of the geologic host of groundwater contamination could be determined at only 33 of the 54 plants in the study group.

Zones were classified according to their average hydraulic conductivity, to provide some indication of the ability of contamination to migrate away from source. Unsaturated zone (soil) contamination was provided a separate classification. Table 3 shows the number of plants at which contamination occurs in each of the three saturated zone classifications (I, II and III, based on average hydraulic conductivity values). The majority of groundwater contamination situations at Alberta sour gas plants seem to occur in zones of moderate hydraulic conductivity (10E-5 < K < 10E-8 m/s), represented by such materials as inter-till clayey sand and silt layers and fractured bedrock, both common in Alberta.

Although directly related to the surficial geology of Alberta, this breakdown did confirm that most groundwater bearing zones which are impacted by sour gas plant operations are not extremely hydraulically conductive. Twenty-six of 32 plants had contamination in groundwater bearing zones whose hydraulic conductivity was less than 10E-5 m/s. This helps to put the situation at Alberta sour gas plants into perspective. In the majority of cases, the estimated advective transport rates of groundwater contamination were not very high, however consideration must also be given to the influences of fracture permeability, contaminant-matrix interactions and the accuracy of hydraulic conductivity data provided in reports. Detailed analysis of contaminant transport rates at the various gas plants was beyond the scope of this study.

TABLE 3
ZONES OF GROUNDWATER CONTAMINATION
Number of Plants with at Least
One Contamination Situation
Occurring in the Indicated Zone
(Total of 32 Surveyed)

Zone	Hydraulic Conductivity Range (m/s)	Number of Plants
II	>10E-05	7
III	10E-05 - 10E-08	20
IV	<10E-08	6

Soil and Unsaturated Zone Contamination

Due to the limited database, firm conclusions regarding the extent of soil and unsaturated zone contamination at Alberta sour gas plants were difficult to make. However, many of the mechanisms leading to groundwater contamination at these facilities necessarily involve the downward migration of contaminants through soil and unsaturated horizons towards shallow groundwater. The results of the limited survey of soil testing data from the six plants are presented in Table 4, and seem to confirm the general conclusion that the frequency of occurrence of soil and unsaturated zone contamination at SGP's will likely be similar to that for groundwater contamination.

TABLE 4
SOIL CONTAMINATION
AT 6 SOUR GAS PLANTS

Contaminant Type	Number of Plants
Hydrocarbons	6
Inorganics	6
Low pH	6
Metals	6

Subsurface Remediation

As part of the first phase of the study, a review of information available regarding subsurface remediation efforts currently being undertaken at Alberta sour gas plants was completed. Information was obtained describing subsurface remediation programs at five facilities. Of these, two were primarily soil remediation operations (plant decommissionings), and three were groundwater remediation schemes currently installed at operating facilities. To date, no other data from remediation programs at sour gas plants has been submitted to Alberta Environment.

Subsurface remediation efforts at Alberta sour gas plants to date have included a variety of techniques. Where geologic conditions were suitable, large diameter passive collection systems have been used to recover free-phase hydrocarbon on the groundwater surface. Attempts to recover free phase condensate in more permeable aquifers using single well pumping schemes have, not unexpectedly, been relatively unsuccessful. Application of dual-pump scavenger-type systems to recover free phase condensate and groundwater separately is being considered at several facilities. Traditional pump and treat methods are being applied for the recovery of groundwater with dissolved contaminants, and the control of plume migration. Deep well injection is the favoured method for disposing of contaminated groundwater.

To date little effort has been devoted to field trials or application of on-site treatment technologies for contaminated groundwater removed by pumping, or to rigorous study of the optimization and proper implementation of pump-and-treat techniques, and the many associated options which exist to enhance the effectiveness of pump-and-treat. The available information also indicates that little attention has been given to the assessment or field testing of newer and more innovative groundwater and soil remediation techniques, which will be discussed briefly in the following sections.

The number of plants at which remediation operations are known to be presently underway is relatively small. In many cases, remedial action has been deemed unnecessary due to geologic conditions and relative isolation of plants, far from any nearby groundwater users, water courses or population centres. In some instances, remediation has been deemed impractical due to limitations of easily available and affordable technology. One consideration to date has undoubtedly been the relatively high cost of subsurface remediation and the fact that at present no regulations or guidelines are available for these operations in Alberta.

The need for clean-up must also be determined. Risk analysis and contaminant transport modelling techniques provide ways of assessing the likelihood of contamination impacting the public or the environment. Results of the risk analysis can then be provided to regulators to ensure a case-by-case assessment of the need for remediation at sour gas plants. Gas processing facilities in the province are found in such diverse locations, and represent such a wide range of hydrogeological and climatic conditions, that application of a single set of rigid criteria to determine the need for clean-up is not recommended. A case-by-case consideration of facilities would help to ensure the economical application of the limited resources. Operators could then direct available funds toward the most serious problems. A joint industry - regulatory approach to these assessments is highly recommended.

3. REMEDIATION TECHNOLOGY REVIEW AND SELECTION

Objectives

The first phase of work laid the necessary foundation to pursue a study of appropriate remedial technologies for Alberta sour gas plants. As the next step towards active field demonstration of appropriate technologies and remedial approaches for the unique conditions present at sour gas plants in Alberta, the second phase of the study was initiated in November of 1990, and is now in progress. The stated objective of this phase is the identification and selection of the most appropriate remediation/treatment technologies for the main types of contamination situations present at Alberta sour gas plants, and the evaluation of new and innovative systems which have significant remediation potential.

The location of many gas plants in the foothills of the Rocky Mountains dictates that much of the geology at these sites will be complex: dipping, faulted and fractured bedrock are common, overburden may consist of permeable glaciofluvial deposits or clay-rich till streaked with more permeable water-bearing sandy layers. Near-surface groundwater in Alberta can be plentiful, and remediation schemes may have to deal with potentially large volumes of water, requiring not only treatment but disposal. Topography and climate are also important considerations.

With these factors in mind, the review of available and promising new remediation technologies is being undertaken within the context of conditions prevalent at Alberta sour gas plants: geological, hydrogeological, climatic, and economic. Also, the review of technologies must not be unnecessarily constrained by the practices of other industries or political jurisdictions where conditions may be different. For these reasons, the study will attempt to balance the academic and the practical viewpoints - time-tested proven technologies as well as new and innovative remediation methods are being reviewed and considered, all within the Alberta sour gas plant frame of reference. Many reviews of remediation technologies have been undertaken over the past few years, and the results of these are available in the literature (including the GASReP reports). This study, however, approaches the question of remediation technology from a fundamentally different direction. Rather than considering the technologies first, and then divining potential applications for them, the study considers tangible, complex problems, and seeks the most appropriate and promising remedial approaches. This procedure simulates in many important ways the challenges being faced ever more frequently by regulators, industry and consultants - how shall a specific site be remediated?

The study is being undertaken by a team of experts from across Canada and the USA, from industry and academia, working with a core of Calgary-based hydrogeologists familiar with Alberta sour gas plants and the special conditions which occur there. The fields of pump-and-treat technology, soil vapour systems, soil remediation, biotechnology, non aqueous phase liquids contaminant hydrogeology, water treatment, barrier and containment technology, and sour gas plant hydrogeology are represented. This team brings to the project a blend of world-wide and local expertise, allowing the broadest possible range of options to be considered, and the most appropriate selected.

Methodology

Based on the results of Phase I, nineteen individual contamination situations, representing the most common and important subsurface conditions at sour gas plants, were identified for consideration. Brief descriptions of each of the 19 contamination situations are provided in Table 5. For each situation, a conceptual model was developed, based on data from gas plants reviewed during Phase I. Based on a comprehensive review of available literature, including all of the latest GASReP reports, and the personal experience of team experts, appropriate and promising technologies for dealing with each situation were identified. At the time of writing, this step was nearing completion.

From this information, short lists of appropriate and promising new/innovative technologies will be assembled, and technologies prioritized. Ranking of choices will be accomplished by a special panel of four experts, each of whom has broad experience in site remediation. The panel will be presented detailed case histories which encompass all 19 contamination situations, and asked to rank choices with the help of a decision matrix system, based on a number of specific criteria. Criteria will include documented successes under similar conditions, expected contaminant removal efficiency, ultimate level of clean-up, capital, operation, maintenance and monitoring costs, equipment availability, ability to operate year-round (in severe winter conditions), and rate of clean-up.

New and innovative technologies which hold promise for remediating contamination at sour gas plants will be assessed on the basis of present status of development/research, published field trials and lab results, theoretical and practical arguments for the suspected suitability of the technology to the particular contamination situation, additional work required to determine applicability, and suggested research options for Alberta sour gas plant applications.

For each contamination situation, a list of new and promising technologies requiring further bench or field scale testing will be compiled, and the most promising of each identified.

Based on the results of the literature review, and the knowledge and experience of the project team, a detailed discussion of the type of data needed for proper design of each recommended technology will be provided. The discussion will include recommended data collection to be done during site assessment, data required from equipment suppliers, and acceptable ranges of uncertainty in the data, presented in the context of the applicable contamination situation. In addition, a set of recommended design criteria for the particular application of the technology will be provided, including such things as accepted limits for the system, sizing of components, pre-treating requirements, typical design pitfalls and errors, and rules of thumb for installation and operation.

Preliminary Findings

At the time of writing, detailed reviews of remedial technologies applicable to the 19 contamination situations were nearing completion. Despite differing experience and areas of specialization, the members of the project team have voiced a few fundamental observations. As expected, the consensus among professionals involved with subsurface remediation is that there is no substitute for individual assessment of each site. A study such as this is useful insofar as it narrows down the possible choices for remediation, but it must be followed

TABLE 5
CONTAMINATION SITUATIONS BEING CONSIDERED

GEOLOGIC HOST OF CONTAMINANTS		CONTAMINANTS		
DESCRIPTION	CODE	CONDENSATE (A)	DISSOLVED ORGANICS INORGANICS (BC)	LOW pH (D)
soils/unsaturated zone moderate-high permeability	(S1)	S1A	S1BC	S1D
soils/unsaturated zone low permability	(S2)	S2A	S2BC	S2D
surficial deposits satuated zone moderate-high K	(T1)	T1A	T1BC	T2D
surficial deposits satuated zone low K	(T2)	T2A	T2BC	T2D
bedrock, high K fractured	(R1)	R1A	R1BC	R1D
bedrock, low K slight-no fracturing	(R2)	R2A	R2BC	R2D
bedrock+surficial deposits in hydraulic connection	(RX)	RXA	-	-

EXAMPLE

A contamination situation exists in which free condensate (CONTAMINANT TYPE A) is present in highly permeable glaciofluvial sands and gravels (HOST TYPE T1).

The resulting contamination situation type would be: T1A

NOTE: K denotes hydraulic conductivity

with detailed site assessment to allow final selection and detailed design and optimization of the system. To date, as discussed above, very few rigorous attempts at remediating subsurface contamination have been undertaken at sour gas plants in Alberta, and virtually no details of such undertakings are available in the literature. From this perspective, the study will provide technical guidance for subsurface remediation efforts at Alberta gas plants. Demonstration of selected technologies will provide a valuable core of research data on which the industry as a whole can base its approach to remediation.

Another commonly held conviction amongst the team is the superiority of on-site treatment of contamination problems, despite the present prevalence of deep-well injection and excavate-and-remove methods. Removal or transfer of contaminated material from one site or medium to another is not seen as a viable long-term solution, either from the regulatory or environmental perspectives. However, the disposal of contaminated water in secure deep formations must remain a practical alternative, and the economics of this method should continue to be assessed against other alternatives, where practical. It is also evident that most solutions to subsurface contamination problems at Alberta sour gas plants will involve several technologies, used either in series or in parallel, or sequentially to move from one level of clean-up to another.

At the time of writing, partial lists of technologies being considered for each of the contamination situations were available. Some of the more promising and innovative suggestions being considered include the use of subsurface volatilization and ventilation systems (SVVS) for the treatment of residual hydrocarbons in both the saturated and unsaturated zones, using the significant quantities of steam and waste heat generated at gas plants to enhance processes such as vapour extraction and volatilization, in- and ex-situ biological methods, and water treatment, using the cold Alberta winters to advantage through freeze crystallization, enhancements to pump-and-treat, advanced oxidation processes, and in-situ sorption technology.

Opportunities for Field Research and Demonstration - Example

As mentioned, one of the intended purposes of the project is to provide opportunities for the demonstration of remedial technologies which could be useful in dealing with the specific contamination situations present at Alberta sour gas plants.

One of the more complex situations being examined involves the presence of free phase condensate and associated dissolved hydrocarbons in the saturated and unsaturated zones of relatively permeable surficial material overlying and in hydraulic connection with fractured bedrock. This type of contamination has been identified at several plants. The scenario encompasses several contamination situations, including X1A/R1A and T1A (condensate in fractured bedrock and overlying surficial materials), S1A (condensate in unsaturated zone and soils), and R1BC/R2BC (dissolved organics in fractured bedrock).

Based on preliminary findings of the expert panel, the most appropriate remedial system for such a situation would involve depression of the groundwater table to expose smeared residual free product, allow skimming of mobile product, and provide hydrodynamic control and elimination of dissolved phase contaminants (BTEX). This would be coupled with vacuum extraction of hydrocarbon vapours, enhanced by injection into the unsaturated zone of air heated using waste heat generated by the plant. Contaminated water produced by pumping would require treatment, and advanced oxidation processes are seen as a prime candidate for demonstration in these circumstances. In addition, the removal of a significant mass of contaminant in the form of vapour would present the opportunity of demonstrating off-gas treatment technologies. The proper application of the pump-and-treat system and its coordination with the vacuum extraction system (and the use of waste heat from the plant) are also areas of potential research.

4. SUMMARY

The need for identification, research and demonstration of applicable subsurface remediation technologies at Alberta sour gas plants has been shown by the results of a detailed survey of 54 such facilities in Alberta. Subsurface contamination at sour gas plants in Alberta is characterized by a wide variety of potential contaminants, complex subsurface conditions, and severe climatic conditions. To date, little work has been done to address the considerable challenges of remediating such contamination, and hence the general level of technology and sophistication which has been applied to these problems is low. This situation presents considerable opportunity not only for development and testing of appropriate solutions for the specific problems discussed, but also for the advancement of research into specific treatment technologies.

A study of remedial technologies applicable to the most common and important subsurface contamination situations at sour gas processing facilities in Alberta is presently underway. The study will identify technologies and approaches worthy of field demonstration at one or more gas plant sites to be selected in 1991. Once the results of this and the parallel effort to solicit formal support of plant operators are available, the Canadian Petroleum Association and Environment Canada will be seeking to contact groups interested in participating in field demonstrations of appropriate remedial technologies. The results of the present study, and the subsequent field demonstrations will be invaluable to the sour gas industry and the cause of environmental protection in general.

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BIOGRAPHICAL SKETCHES

Paul Hardisty obtained a Bachelor's degree in Geological Engineering from the University of British Columbia, and an MSc in Engineering Hydrology (Groundwater Engineering) from Imperial College, University of London, England, where he is presently enroled as a PhD candidate studying the behaviour of hydrocarbons in groundwater. Mr. Hardisty is a Senior Hydrogeologist with Piteau Engineering Ltd. in Calgary, Canada, and is currently involved in several large scale groundwater remediation projects. His overseas experience has included work in Turkey, Ghana, Ivory Coast, and Ethiopia. His interests include LNAPL and aqueous phase behaviour in complex hydrogeological systems, groundwater flow in fractured media, and fractal geometry.

Dr. Tadeusz Dabrowski obtained a Master's degree in Natural Sciences (hydrogeology) from the University of Warsaw and a PhD in hydrogeology from the Polish Academy of Sciences before emigrating to Canada. Dr. Dabrowski is president and principal hydrogeologist of Piteau Engineering Ltd., and has over 30 years of experience in petroleum industry related groundwater studies. He has been involved in assessments of groundwater contamination at over sixty major refineries and gas plants in Canada and overseas, and was appointed by the Alberta Minister of Environment to the task force evaluating the impact of sour gas plant operations on groundwater in southwestern Alberta. Dr. Dabrowski has extensive experience as an expert witness and reviewer in cases involving groundwater contamination.

THE INFLUENCE OF METHANOL AND MTBE ON THE FATE AND PERSISTENCE OF MONOAROMATIC HYDROCARBONS IN GROUNDWATER

by

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EXTENDED ABSTRACT

The monoaromatic hydrocarbons in gasoline represents a significant, potential source of groundwater contamination. They include benzene, toluene, ethylbenzene and the three xylenes, m-, o- and p-, as a group termed BTEX. These constitute the most soluble, most mobile fraction of gasoline and benzene especially has a very low standard in drinking water of 5 ug/L. Currently, many oxygen-bearing organics (oxygenates) such as alcohols and ethers are added to gasoline to boost octane and to reduce air pollution from combustion. The use of oxygenates may increase in response to concern about urban air quality. Little is known about the impacts of these oxygenates on the groundwater environment.

Oxygenates are highly soluble and so they can be anticipated to occur at higher concentrations than even BTEX in oxygenate/gasoline-impacted groundwaters. Highly soluble compounds have a low sorption potential, so oxygenates should be more mobile in groundwater than BTEX. Oxygenates, when present at high concentrations could decrease the sorptive retardation of BTEX via cosolvent effects which could lead to enhanced mobility of BTEX in groundwater. The oxygenate could be biodegraded in preference to BTEX and so could consume the oxygen required for BTEX biodegradation. Alternately, the oxygenate could be toxic or inhibitory to BTEX-degraders.

The current study considers two, common oxygenates: methanol and methyl-tertiary-butyl-ether (MTBE). Up to 10% MTBE is currently added to gasoline to boost octane rating. Methanol, in particular a mixture of 85% methanol and 15% gasoline, termed M-85, has been proposed as a fuel to reduce air pollution. MTBE has a solubility of about 48,000 mg/L and methanol is miscible with water.

The current research program has these objectives:

1) to determine under what conditions the presence of methanol and MTBE enhances the solubility of BTEX in groundwaters contaminated by a subsurface release of gasoline
2) to determine the effects of methanol and MTBE on BTEX migration and persistence in groundwater
3) to describe the fate of methanol and MTBE in groundwater

Details of the results will be available from API reports, from a paper published in the Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water, Houston, Oct. 31 - Nov. 2, 1990, and in the M Sc thesis by Hubbard (Univ. of Waterloo, in prep.). Some of the preliminary results and interpretations are presented here. The research is supported by the American Petroleum Institute and by the Ontario University Research Incentive Fund.

Laboratory equilibrium partitioning experiments confirmed that up to 15% MTBE in gasoline is unlikely to produce enhanced solubility of BTEX in impacted groundwaters. With methanol, the aqueous BTEX concentrations were significantly enhanced as the methanol concentration in the aqueous phase exceeded about 20%. Such conditions are likely restricted to gasolines with high contents of alcohols such as methanol and only for high effective ratios of contacting gasoline to groundwater.

In a spill, equilibrium between methanol-bearing gasoline and groundwater is likely only between gasoline and small volumes of groundwater at the interface. The effective gasoline:groundwater ratio in contact is unknown. Groundwater flowing around or through the gasoline residual may bring successive batches of uncontaminated groundwater into equilibrium with the residual gasoline. The initial groundwater will remove most of the methanol and a higher proportion of BTEX than subsequent batches of groundwater which are equilibrating with a gasoline residual increasingly depleted in methanol and BTEX. The dissolved plumes that could result from various scenarios were simulated. The methanol content of the gasoline was either 0%, 50% or 85% and batches of groundwater successively equilibrating with these gasolines had ratios of gasoline:water of 0.1, 1.0 and 10. Each batch of equilibrated water was assumed to move off laterally due to the groundwater flow.

The simulation considered only dissolved methanol and benzene concentrations. Dissolved methanol was assumed to migrate at the same rate as the groundwater, while benzene moved at about 90% of the groundwater velocity. The groundwater was assumed to move horizontally at about 10 cm per day. The simulation aquifer and flow field resembled the shallow Borden sand aquifer. The plume of contaminated groundwater from M-85 where the gasoline:groundwater ratio exceeded 1:10 had a very high methanol content (> 30%) and elevated benzene concentrations (> 700 mg/L) at the leading edge. Methanol was quickly dissolved so the pulse of methanol in the groundwater was relatively short-lived. Benzene concentrations gradually declined over time. Compared to a simulated plume resulting from gasoline without methanol, the plume from M-85 had much higher benzene concentrations initially, but the source was more rapidly depleted in benzene, so the pulse of unacceptably high benzene concentrations would be shorter. The most significant parameters controlling the nature of the dissolved plume were the initial gasoline:groundwater ratios in equilibrium and the methanol content of the gasoline.

A natural gradient injection experiment has been preformed at CFB Borden to investigate the influence of methanol and MTBE on the behaviour of the dissolved BTEX in groundwater. The experimental zone is in a 5-meter lens of aerobic, uncontaminated groundwater which overlies the leachate plume. The site has been used for previous natural gradient experiments so the hydrogeology is well understood. The medium to fine sand has small-scale layering and heterogeneities. The groundwater flows essentially horizontally at an average velocity of 0.09 m/day.

Dissolved contaminants were injected below the water table to represent dissolved plumes which might emanate from subsurface contamination by normal gasoline (PS-6, supplied by API), gasoline with 15% MTBE, and M-85. The three plumes were injected simultaneously, side-by-side, so that they would all encounter the same degree of aquifer heterogeneity, would flow at about the same rate and in the same biogeochemical environment. Injection took place on July 13, 1988 and groundwater monitoring continued for about 480 days. Three long, thin slugs of contaminated groundwater with minimal lateral overlap were created. The average injection concentrations were:

Plume:	PS-6 Only	85% Methanol	15% MTBE
Solute	Average Concentrations (mg/L)		
Chloride	478	577	515
Methanol		7030	
MTBE			289
Benzene	7.2	7.7	7.7
Toluene	5.0	5.2	5.3
Ethylbenzene	0.8	0.8	1.0
p-Xylene	0.8	0.8	1.0
m-Xylene	2.0	2.1	2.5
0-Xylene	1.2	1.2	1.4
Total BTEX	17.0	17.8	18.4

The transport of the solutes in groundwater was monitored by sampling from a detailed piezometer network for the solutes and for dissolved oxygen. Six sampling "snapshots" were taken over the 476 day experiment, with the collection and analysis of 850 to 1600 samples each time.

Figure 1 shows the distribution of chloride, oxygenates, benzene and p-xylene at 6 and 318 days (399 days for p-xylene) after injection. The contours are of vertically integrated concentration data and are shown only to indicate the position of the solute plumes. In detail the migration is more complex, reflecting the small-scale heterogeneities in the Borden aquifer. Clearly, all solutes are migrating and dispersing, with longitudinal dispersion or spreading far exceeding transverse dispersion. The oxygenates are migrating at essentially the same rate as groundwater and the conservative solute, chloride. Benzene is somewhat retarded and p-xylene is more retarded, as anticipated.

The mass loss for each organic over time has been assessed but this analysis is being refined. Table 1 gives the preliminary estimates of total mass for each solute injected and in each plume at days 6, 46, 106 and 476 after injection. The chloride decline indicates either a poor approximation of the distribution or that some of the chloride mass lies outside the sampled network. In any event, the declines in the organics can still be appreciated. By day 476, chloride mass has declined to about 50% of that estimated to have been injected. All monoaromatics have declined to less that 20% of the initial mass; all except benzene have declined to less than 10% of their initial mass. Methanol declined to about 16% of the initial mass, while MTBE has declined only to about 37% of the initial mass. The MTBE decline in mass is not much beyond that for chloride, indicating its recalcitrance relative to the other organics.

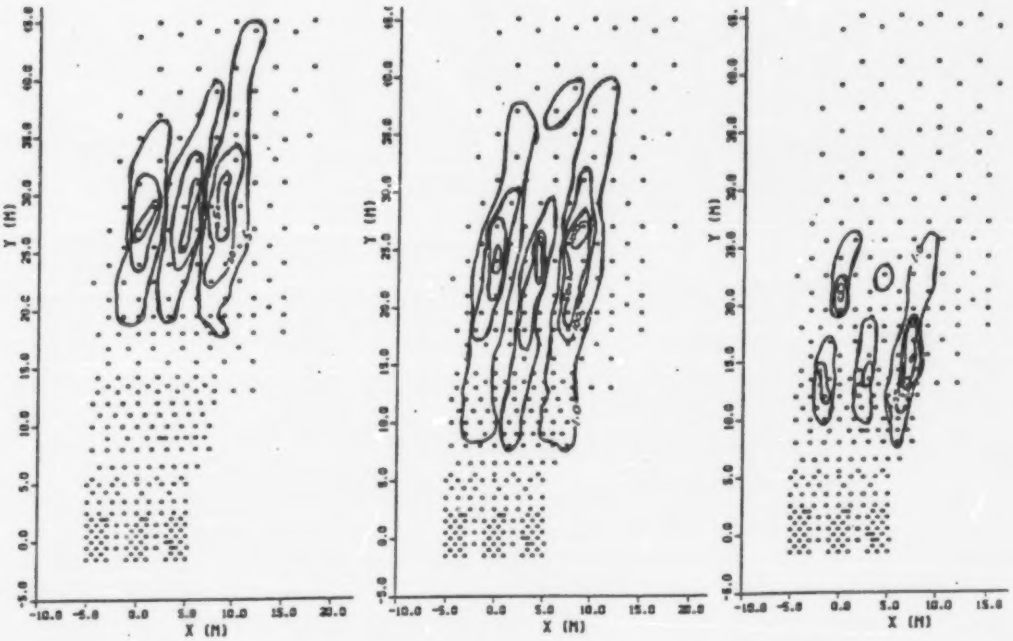
Table 1. Estimates of the mass of each solute injected and in each plume at selected days after injection.

	Injected	Day 6	Day 42	Day 106	Day 476
Solute			Mass (g)		
		MTBE PLUME			
Chloride	1460	1360	920	800	750
MTBE	820	670	540	440	300
Benzene	21.8	18.9	16.2	10.3	2.3
Toluene	15.2	11.6	11.3	4.8	0.15
m-Xylene	7.0	4.3	3.9	1.3	0.00
p-Xylene	2.7	1.7	1.7	0.84	0.10
		METHANOL PLUME			
Chloride	1640	1200	790	1090	750
Methanol	19900	10900	7400	10300	3.1
Benzene	21.9	13.1	8.9	11.6	4.3
Toluene	14.6	8.5	6.3	6.3	0.08
m-Xylene	5.9	3.1	2.9	1.4	0.05
p-Xylene	2.3	1.3	1.1	0.64	0.29
		PS-6 PLUME			
Chloride	1400	820	880	690	650
Benzene	20.4	13.8	13.4	8.1	2.1
Toluene	14.0	8.6	7.9	4.9	0.05
m-Xylene	5.8	3.5	3.7	1.6	0.004
p-Xylene	2.3	1.4	1.4	0.86	0.06

Although by day 476 most of the methanol had been biodegraded, the BTEX in the methanol plume were at higher relative concentrations than in the MTBE or PS-6 plumes. This suggests that methanol slowed the BTEX biodegradation rate compared to oxygenate-free or MTBE-containing groundwater. Laboratory experiments found no significant biodegradation of BTEX in the presence of 7000 mg/L methanol but some BTEX biodegradation was noted when the methanol concentration was only 1000 mg/L. In the field experiment, dilution and different rates of migration bring about continuously lowering methanol concentration in waters containing BTEX. Thus, while initially methanol could be inhibiting BTEX biodegradation, lowering methanol concentrations could permit subsequent BTEX biodegradation. On the other hand, as methanol itself is biodegraded and oxygen is consumed, BTEX biodegradation could still be inhibited by lack of oxygen. Biodegradation of only a small proportion of the 7000 mg/L of methanol present in the injected water would consume all the available dissolved oxygen, thus inhibiting aerobic biodegradation of BTEX. In fact it appears that the removal of methanol aerobically would require much more oxygen than is available in the methanol-impacted groundwater. The possibility of anaerobic methanol biodegradation needs to be considered.

Methanol was essentially removed from the groundwater by 476 days. MTBE, on the other hand, appeared to be essentially recalcitrant. BTEX was biodegraded as anticipated in both the gasoline plume and the MTBE plume at a faster rate than in the methanol plume. It is tentatively concluded that the mechanism for greater BTEX persistence with methanol being present is the initial inhibition of BTEX biodegradation by high methanol concentrations and then inhibition due to removal of oxygen by methanol biodegradation. Again, an examination of the distribution of dissolved oxygen in the M-85 plume is underway and should clarify this issue.

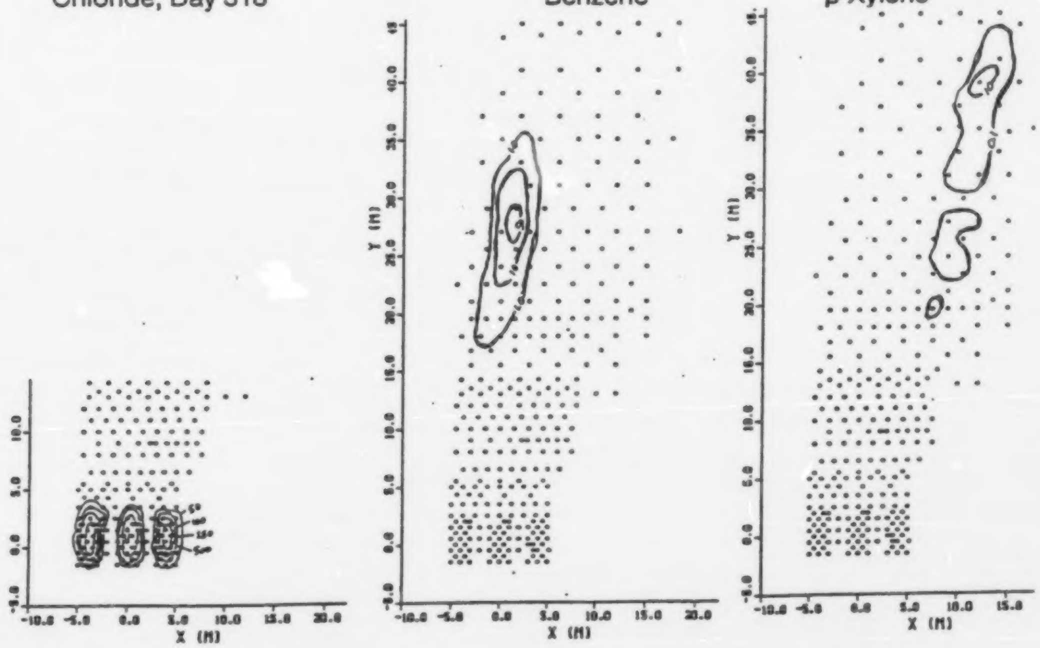
Overall, the impact of oxygenates such as MTBE and methanol on groundwater contamination is serious and complex. The replacement of BTEX by oxygenates will provide a lower total load of these contaminants to the groundwater and so should lessen their impact. Enhanced solubility of BTEX will likely be found only with high methanol gasolines where the effective gasoline:water ratio in contact is relatively high. Once dissolved, the oxygenates will be very mobile and MTBE appears to be especially persistent. Methanol appears to biodegrade, but in so doing it appears to enhance the persistence of BTEX. Thus the consequences for groundwater contamination of the increased use of MTBE and methanol in gasoline are both positive and negative. Those dealing with groundwater contamination will be faced with a much more complex groundwater problem than simple gasoline has produced in the past. Much more research is required to prepare the appropriate response.



Chloride, Day 318

Benzene

p-Xylene



Chloride, Day 6

MTBE

Methanol

Figure 1. The distribution of selected solutes in groundwater about 318 days after injection (chloride also at 6 days to show initial distribution of all solutes). The vertically integrated concentrations are contoured and presented in plan view. Groundwater flow is upwards and slightly to the left. Dots are multilevel monitoring wells.

STATISTICAL METHOD DEVELOPED BY THE AMERICAN PETROLEUM INSTITUTE TO EVALUATE THE TECHNICAL LIMITS OF A GROUNDWATER REMEDIATION PROJECT

by

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Historically, project managers have observed that, while initially successful in decreasing dissolved hydrocarbons in groundwater, pump-and-treat technology can show decreasing efficiency for groundwater remediation with time. In response, the API Groundwater Technical Task Force (GWTTF) Force contracted with Hunter/ESE to develop a statistical tool to evaluate subsurface hydrocarbon remediations.

Usually during remediations, the concentrations of organic contaminants show a rapid decline (Zone 1 on Figure 1) and then level off reaching an asymptotic phase (Zone 2 on Figure 1). The contaminant concentrations remaining at this asymptotic phase are often above the regulatory remediation level (RRL). USEPA recently published a review of ongoing pump-and-treat remediations outlining this pattern (USEPA, 1989).

This leads to a situation where, at a minimum, long-term pumping is required to attempt to satisfy the RRL (Figure 2). And, realistically, the RRL may never be reached using pump-and-treat technology. This is a direct reflection of the limitations of pump-and-treat technologies.

Pump-and-treat technology is most effective for two purposes during organic contamination remediation. First, it is very effective for groundwater depth and gradient control. And, it can be effective for free-phase hydrocarbon recovery. However, it is usually not effective for remediation of residual hydrocarbons either adsorbed to soil particles or trapped in soil pores.

Figure 1 represents the commonly observed response of dissolved hydrocarbon concentrations during a pump-and-treat remediation. The response in Zone 1 reflects removal of free-phase hydrocarbons and/or existing dissolved contamination. It also results from drawing uncontaminated water into the remediation area. The response in Zone 2 reflects residual soil contamination releasing hydrocarbons to groundwater at a rate nearly equal to that of the remediation removal.

Several responses are possible when the asymptotic phase has been reached. The existing remediation technique can continue, the remediation technique can be modified, or the remediation can be discontinued. Continuing with the existing remediation technology may be acceptable where the time required to complete is not important. However, the action most often taken is modification or amendment of the existing technology to address residual soil contamination that serves as the source of groundwater contamination. But, technology modification may not always be the alternative required.

In some situations, simply turning the existing system off and monitoring groundwater is a valid alternative. This approach is most applicable in locations where groundwater is not usable and/or where the remaining hydrocarbon levels are low enough that they may be expected to remediate naturally. As shown in the Benzene in Florida Groundwater Study (Florida Petroleum Council, 1986) remediation did not enhance the rate of benzene removal beyond that expected to result naturally when benzene concentrations in groundwater reached 100 ppb. Thus, remediation system shutdown and subsequent groundwater monitoring can be an acceptable response.

As shown in Figure 3, the data within an asymptotic phase can include significant variability resulting from sampling and/or analytical error, seasonal effects, or system malfunction. Thus, the project manager may not feel confident that a remediation has reached the asymptotic phase and requires modification.

To develop the method, the GWTTF and Hunter/ESE, Inc evaluated real data from pump-and-treat remediations. Two alternative statistical approaches were evaluated on seven data sets; a linear regression analysis and a first-order exponential decay. For five of the seven data sets evaluated, the linear regression was significantly more powerful and could identify the asymptotic phase using less data. For both techniques, a remediation was considered in the asymptotic phase if the slope of the line of concentration versus time was not significantly different from zero.

Based on the study results, a software program was developed that looks back in time from the most recent data point to determine whether remediation has reached the asymptotic phase. It can be applied at any time after initiation of a remediation in which hydrocarbon concentrations have been measured five times. In practice, ten measurements spaced over a period of six to nine months are required to give accurate results.

The program can be re-applied as additional measurements are made available and can be used to extrapolate into the future to estimate when specific numerical levels may be reached. However, the validity of this extrapolation is limited by the quality of the data.

The current study results and computer package written in SAS will be available through API in late February, 1991. An additional PC version will be available in late second quarter, 1991.

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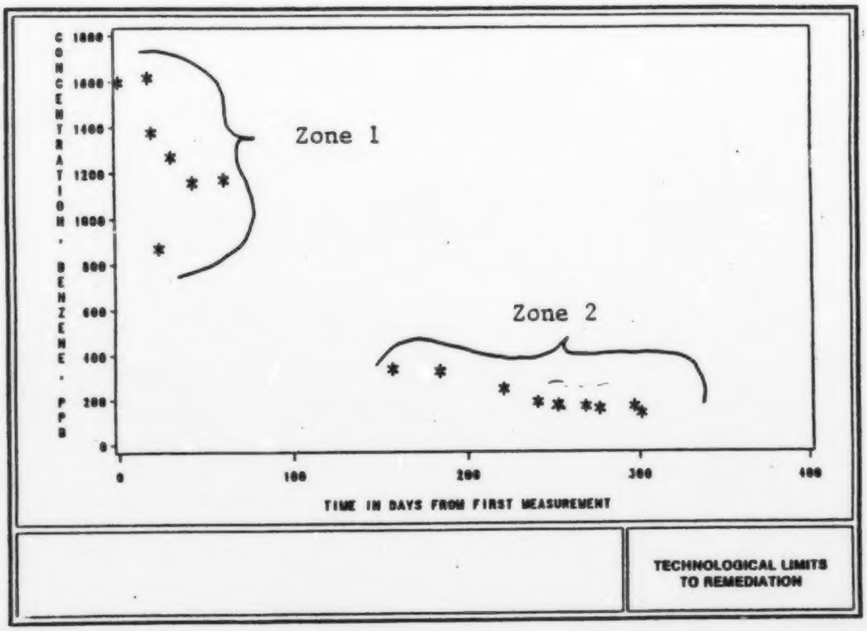

Figure 1: Benzene concentrations in groundwater versus time (API, 1991).

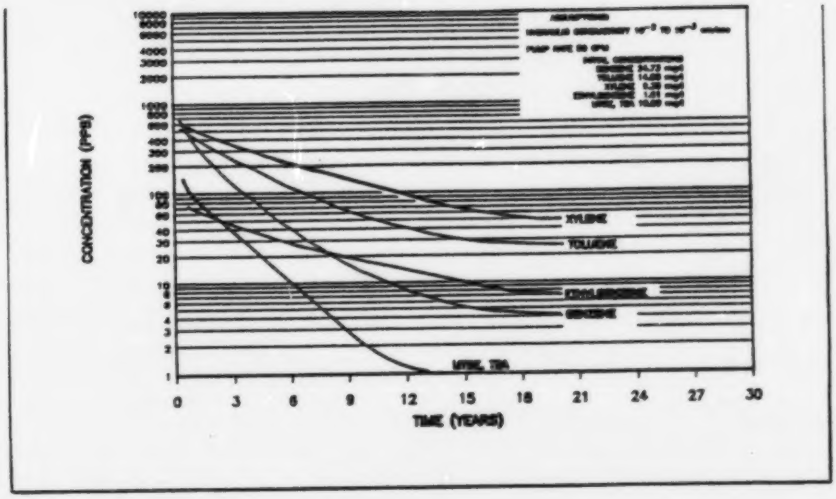

Figure 2: Time in years required to remediate a coarse sand type aquifer using pump and treat (modified from Figure 5.3 in API, 1986).

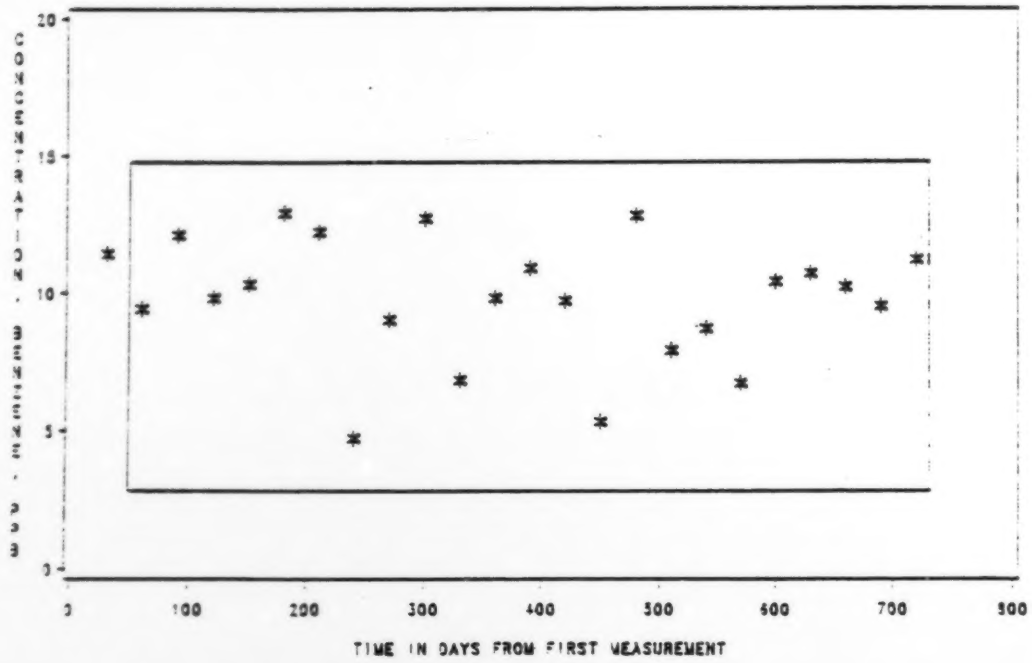

Figure 3: Data variability within an asymptotic phase (API, 1991)

USEPA Ground-Water Initiative
Improvement of Pump and Treat Remediation

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January 30, 1991

Introduction

A pump and treat system remediates a contaminated aquifer by extracting contaminated water from the aquifer, treating the contaminated water on the surface, and discharging the cleaned water. Pump and treat systems are designed with two objectives in mind:

(1) to use the hydraulic gradients created by the pumping system to prevent further spread of the contaminant plume, and
(2) to reduce the concentration of the pollutants in the aquifer below a predetermined limit.

In order for a pump and treat system to successfully remediate an aquifer, two conditions must be met. First, the contaminants to be removed must be in solution. Second, the pumped water must pass through those regions of the aquifer in which the contaminants are located. If either one of these conditions is not fully met, the efficiency of the pump and treat system will be greatly reduced.

Experience has shown that while pump and treat may often be the most viable option for aquifer remediation, pump and treat systems frequently fail to meet their original design goals. As a result, pump and treat remediation has tended to require much more time, and be much more expensive, than was anticipated when the systems were designed and placed in operation. The Subsurface Cleanup and Mobilization Processes (SCAMP) initiative is a US Environmental Protection Agency (USEPA) funded effort to improve the efficacy of pump and treat remedial actions at contaminated sites.

Early evidence that pump and treat remediation systems were not meeting their design specifications was largely anecdotal in nature, based on reports of remedial project managers and other individuals working at sites where these systems were in operation. Many of these reports were in the form of requests for assistance from the USEPA's Robert S. Kerr Environmental Research Laboratory's (RSKERL) Superfund Technical

Support Center, which provides technical expertise for ground-water related problems. The RSKERL is the USEPA's principal research center for problems related to the prevention and remediation of ground-water contamination. Laboratory soil column experiments at the RSKERL provided qualitative insights into some of the reasons for these problems, and supported the idea that pump and treat remediation would be more difficult than had originally been envisioned.

In 1989 the USEPA's Superfund Program conducted a formal study (USEPA, 1990) to document the extent and nature of the problems with pump and treat remediation. The study began with 112 candidate sites in the Superfund, RCRA, and state remediation programs. Of these 112, nineteen were selected for more detailed study. The nineteen were those for which adequate data was thought to be available to make an informed judgement about the operation of the pump and treat system at the site. Twelve of the nineteen sites had restoration of ground-water quality, usually to USEPA drinking water standards, as one goal of the remedial action. One of the twelve claimed to have reached that goal, but provided little hard evidence to back up the claim.

The typical system in the study would initially remove a large mass of contaminant which would, in turn, lead to a concomitant initial drop in the concentration of the contaminant in the ground water at the site. After this initial drop the concentration of the contaminant would tend to level off at, or only slowly decrease from, a concentration well in excess of the original design goal. It should also be noted that as a result of the hydraulic control provided by the pumping system, the remedial actions were largely effective at preventing further spread of the contaminant plume. However, the continued high concentration of the contaminants in the plume meant that the pumping system, in many cases, would have to be kept in operation for very long periods of time if the contaminants were to be kept from spreading.

The most common, and serious, problems identified in the 1989 study were related to:

(1) aquifer heterogeneity,
(2) interactions of the contaminants with the geologic matrix, particularly as a result of sorption phenomena, and
(3) the presence of a separate immiscible fluid phase in the plume.

Each of these phenomena is a barrier to the success of a pump and treat remediation. If it is present, it must be identified and overcome before the remedial action can succeed.

At many of the study sites, one, or more, of these three phenomena was not identified during the site characterization phase of the remediation project, and consequently was not considered in designing the pump and treat project. Failure to account for the phenomenon in the system design was at least part of the reason that the system, when operating, did not meet its original design goal. This was particularly true for the presence of a separate immiscible liquid phase. Even if the problem had been recognized, however, there was, and is, often no good option for dealing with it. As a result, the EPA recognized a need for further research on pump and treat remediation.

SCAMP Initiative

In the spring of 1989, the Robert S. Kerr Environmental Research Laboratory and the Superfund Program Office developed a funding initiative whose goal was to improve the efficacy of pump and treat remedial actions. The initiative emphasized the "pump" half of "pump and treat" since this is where the major problems exist at the present time. The initiative was given the acronym "SCAMP" for Subsurface Cleanup and Mobilization Processes.

Specific objectives of the SCAMP initiative are to:

(1) provide remedial project managers with improved decision-making tools to (a) determine when pump and treat is a good option for remediation, (b) decide what steps should be taken to improve the outcome of a pump and treat remedial action, and (c) be able to make reliable estimates of the outcome of a pump and treat remedial action;
(2) develop and evaluate improved methods for site characterization;
(3) develop and evaluate techniques to accelerate pump and treat remedial actions; and
(4) develop an improved, quantitative, understanding of the processes controlling the efficacy of pump and treat remedial actions.

Research funded by this initiative will be designed to meet these objectives and will begin during the 1991 fiscal year (beginning in

October 1990). SCAMP is planned to continue for five years. The initial funding level was $1.07M per year.

The audience for the outputs of the SCAMP research program will include:

(1) the remediation management community, particularly those individuals in the EPA and other agencies with direct responsibility for the remediation of specific sites,
(2) the remediation policy community, particularly the EPA Superfund program headquarters staff and Regional EPA Superfund program managers,
(3) the science and engineering research community, and
(4) engineering firms and remediation contractors.

Technical assistance and technology transfer activities are built into the program. These activities will largely be the responsibility of the RSKERL's Superfund Technology Support Center.

A meeting to start the planning process for SCAMP research was held at the RSKERL in August 1990. Attendees at the meeting included both EPA personnel and experts from outside the Agency. The meeting was not designed to plan specific projects, but rather to determine where to place the emphasis of the SCAMP research. One recommendation of the meeting was that with the limited amount of money available, the research would be most effective if placed on a specific problem. The recommended area was remediation of sites contaminated by dense non-aqueous phase liquids (DNAPL's). These sites are among the most commonly occurring and the most difficult to effectively remediate. The attendees also recommended that the research emphasize means to accelerate pump and treat remediation and site characterization, particularly for sites with complex hydrogeological settings such as fractured rock. At the present time, a research plan incorporating these ideas is nearing completion.

Planned Research - FY 1991, FY 1992

For fiscal years 1991 and 1992, specific SCAMP research projects in the area of site characterization for DNAPL contaminated sites will emphasize:

(1) understanding the implications of site characteristics for the success or failure of pump and treat remedial actions;

(2) better ways to characterize sites with complex hydrogeology, particularly fractured rock or strongly layered geologic settings;
(3) measuring and describing the three-dimensional distribution of the contaminants at a site; and
(4) the basic fate and transport process research required to support the proposed site characterization research.

SCAMP research for fiscal years 1991 and 1992 in the area of accelerated remediation technology will emphasize the use of surfactants and solvents. Specific activities are likely to include:

(1) determining the current state-of-the-technology;
(2) research on improved systems to deliver surfactants and solvents to the regions of the aquifer where they are needed;
(3) determining the characteristics of acceptable agents both in terms of their efficacy and their acceptability for injection into an actual or potential source of drinking water;
(4) tests of accelerated remediation scenarios using large-scale physical models; and
(5) the basic fate and transport process research required to support the proposed accelerated-remediation research.

On a percentage basis. the SCAMP research effort for FY 1991 and FY 1992 is expected to be broken out roughly as:

30% Surfactants
10% Mixed solvents
20% Complex hydrogeology
20% Physical model demonstration/evaluation
20% Site characterization

This breakout is based on the perceived importance of the specific areas for improving the efficacy of pump and treat, the recommendations of the planning meeting, and the existence of funding for related research by the USEPA and other agencies.

Longer term research plans will include field tests of the site characterization and accelerated remediation technologies, and the evaluation of additional technologies to accelerate pump and treat remediation.

TOTAL P. 7

Disclaimer

Although the information in this document has been funded by the United States Environmental Protection Agency, it has not been subject to the Agency's peer and administrative review process. It does not necessarily represent the views of the Agency and no official endorsement should be inferred.

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Bioremediation Field Performance Evaluation Initiative

Walter Kovalick
U. S. EPA Technology Innovation Office
Washington, D.C.

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